Electronic Supplementary Material (ESI) for ChemComm.

Supplementary data

Dual-Catalyzed Boryldifluoroallylation of Alkynes: Efficient Method for Synthesis of Skipped *gem*-Difluorodienes

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1. General Information

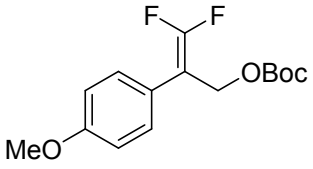
1.1.Materials

All solvents were purchased and used without further purification. The following Chemicals were purchased and used as received: CuCl (Acros), LiO^{t}Bu (99%, J&K), KO^{t}Bu (99%, Acros), NaO^{t}Bu (99%, Acros), dry THF (J&K). Alkynes and *gem*-difluoroallyl tert-butyl carbonates were obtained from commercial suppliers or prepared according to standard procedures.

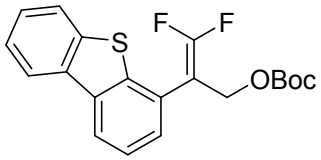
1.2. Analytical Methods

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400 MHz spectrometer at 295 K in $CDCl_3$ unless otherwise noted. Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR were reported as follows: chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Data for ^{19}F NMR were reported as follows:chemical shift (δ ppm), multiplicity, coupling constant (Hz). Chemical shifts were reported using the residual solvent $CHCl_3$ as the internal reference for ^{1}H NMR (δ =7.260 ppm) and $CDCl_3$ peak as the internal reference for ^{13}C NMR (δ = 77.16 ppm). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2010 plus Series GC system equipped with a flame-ionization detector. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (300-400 mesh).

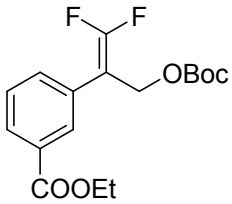
2. Preparation of *gem*-difluoroallyl tert-butyl carbonate



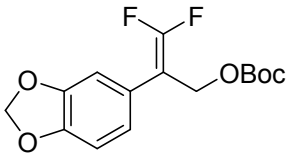
2a



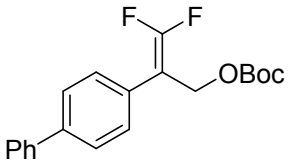
2e



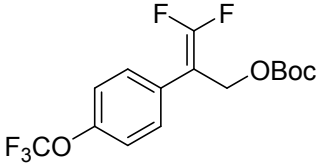
2f



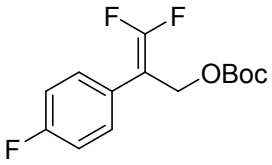
2g



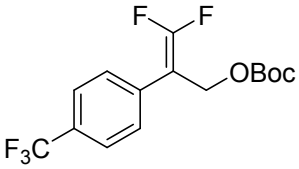
2h



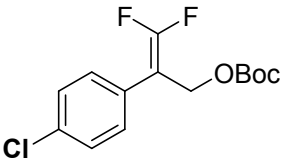
2i



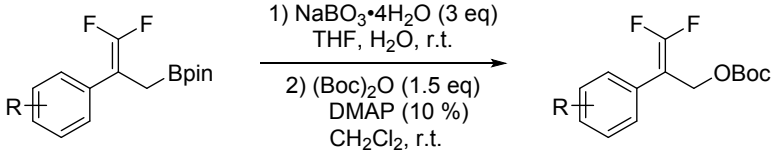
2j



2k



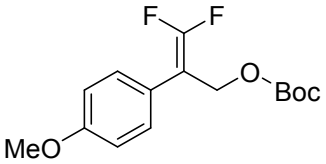
2l



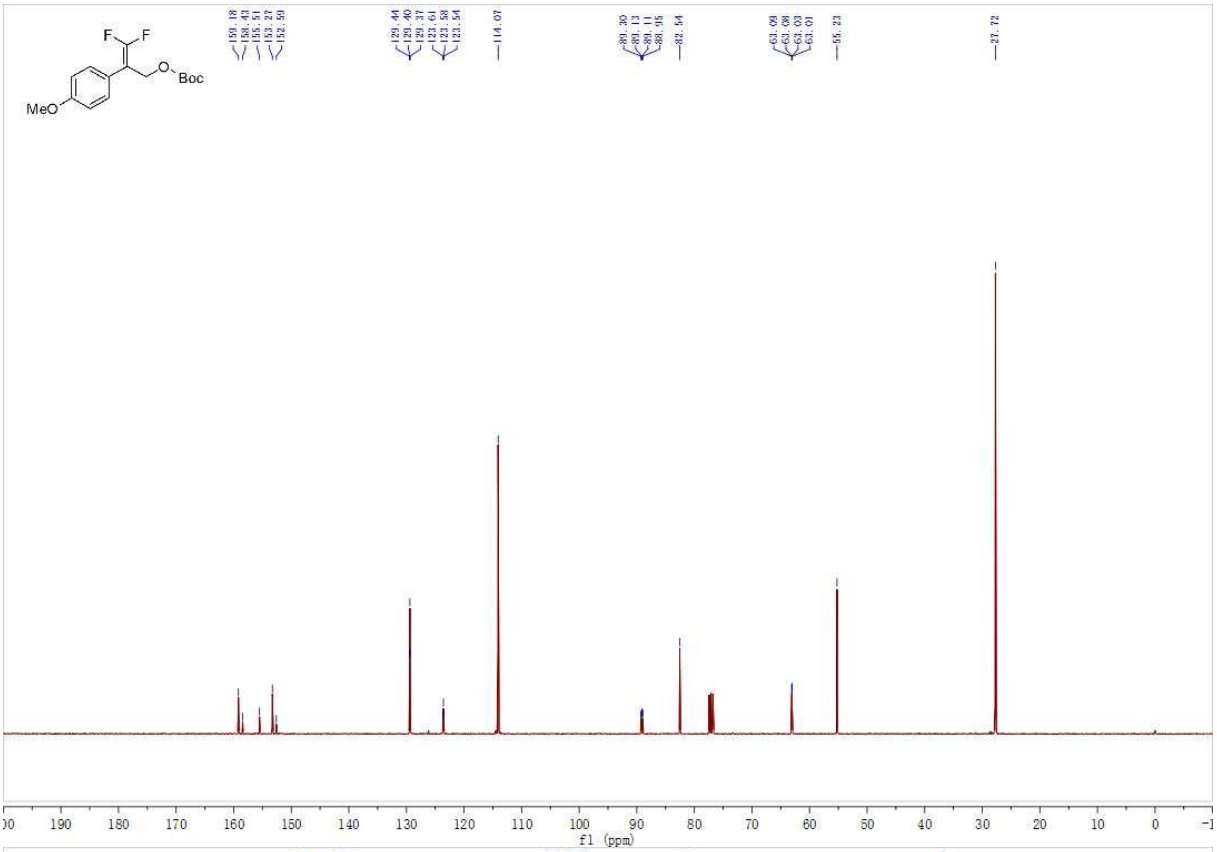
To a Schlenk tube equipped with a magnetic stir bar were added $NaBO_3 \cdot 4H_2O$ (3 eq), *gem*-difluoroallylboronates[1] (10 mmol), THF (10 mL) and H_2O (10 mL). The resulting solution was stirred at room temperature for 20 min. Then Et_2O and water were added and the layers were separated. The aqueous phase was extracted with Et_2O (x 2) and the combined organic layers were dried over Na_2SO_4 and concentrated to give crude product *gem*-difluoroallyl alcohol without any purification.

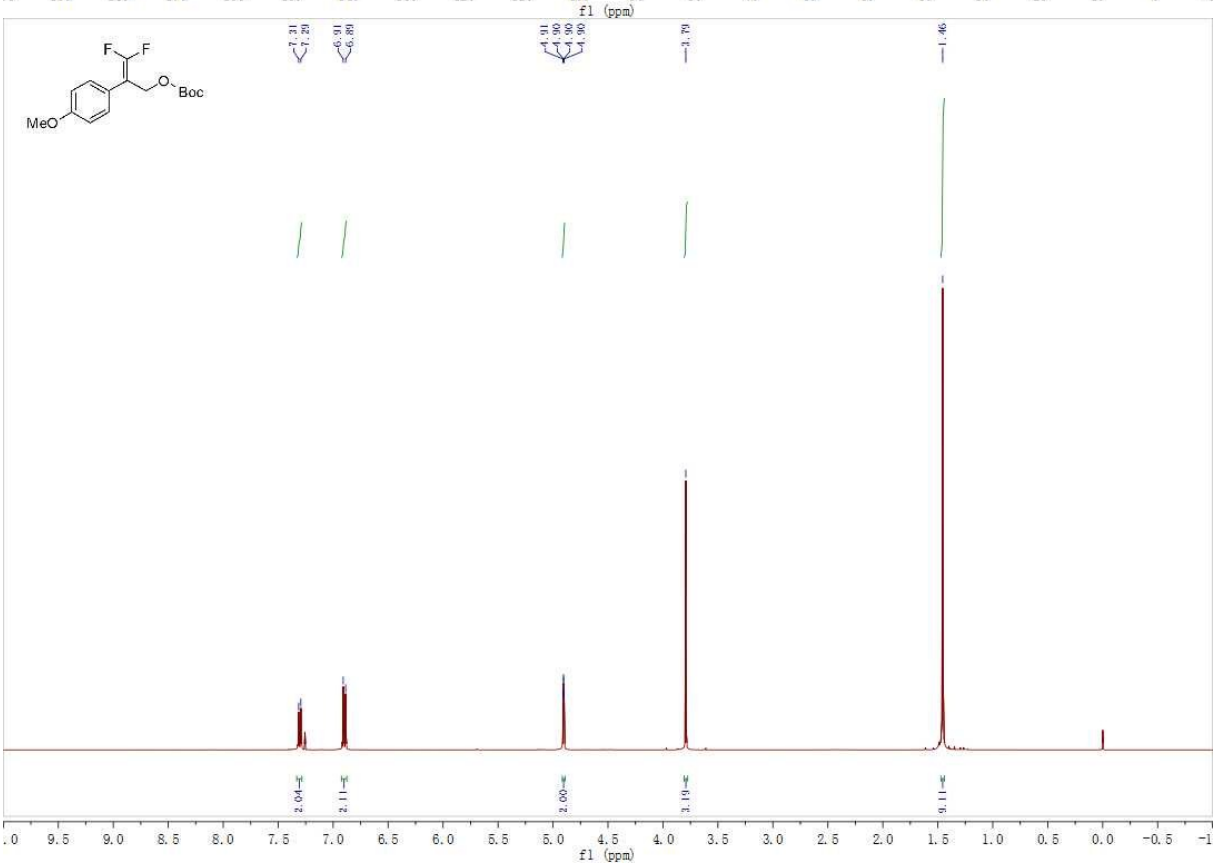
To a solution of *gem*-difluoroallyl alcohol in CH_2Cl_2 (10 mL) were added di-tert-butyl dicarbonate (1.92 g, 15 mmol). Then N,N-dimethylpyridin-4-mine(122.2 mg, 1 mmol) was added to the mixture. The resulting solution was stirred at room temperature for 10 min. Then Et_2O and water were added and the layers were separated. The aqueous phase was extracted with Et_2O (x 2) and the combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel to give the product.

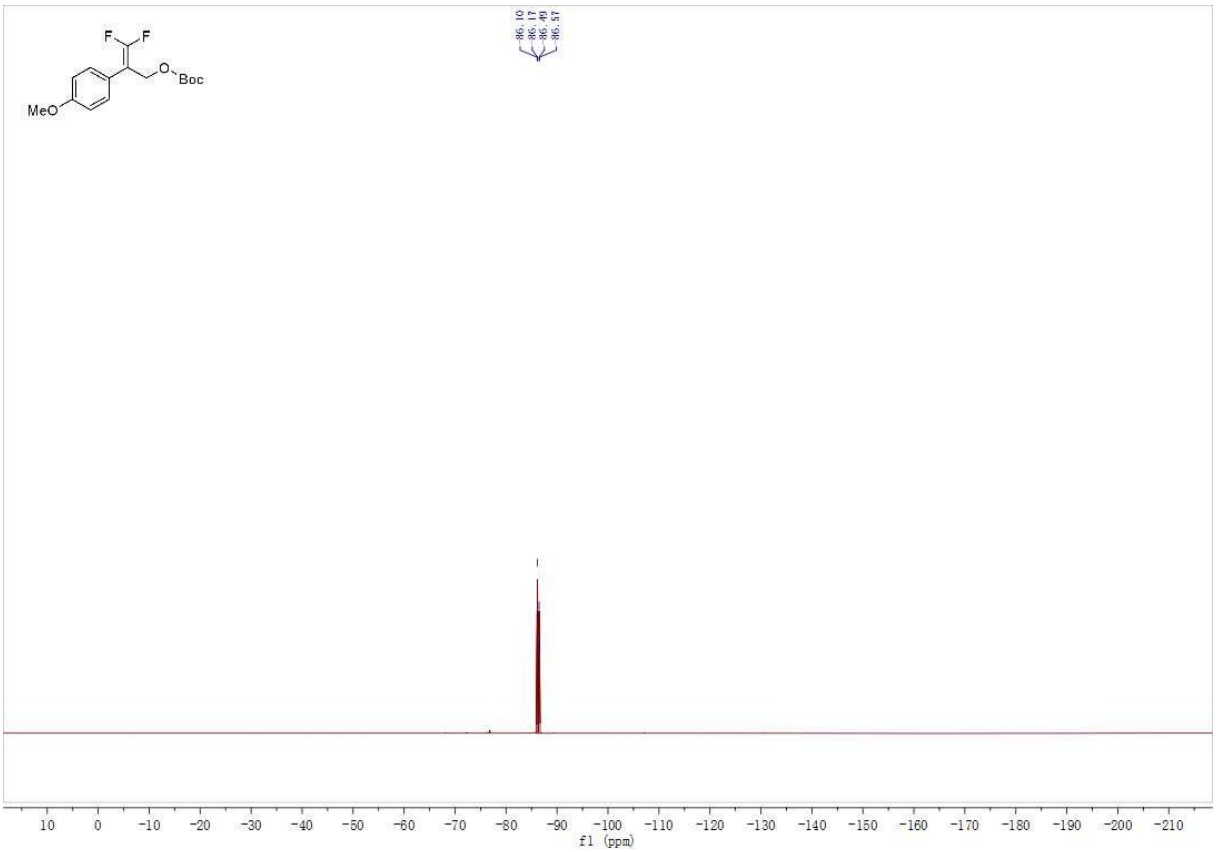
tert-butyl (3,3-difluoro-2-(4-methoxyphenyl)allyl) carbonate (2a)



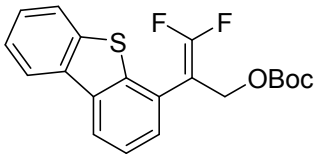
Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (50:1) as thick oil (1.9 g, 58 %) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 4.90 (s, 2H), 3.79 (s, 3H), 1.46 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.18, 155.51 (dd, *J* = 296.94, 295.93 Hz), 153.27, 129.40, 123.58, 114.07, 89.12 (dd, *J* = 18.6, 16.7 Hz), 82.54, 63.03, 55.23, 27.72. ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.14 (d, *J* = 28.6 Hz), -86.53 (d, *J* = 28.6 Hz). HRMS (ESI^+): Calcd for $C_{15}H_{18}F_2O_4$ $[Na]^+$: 323.1071, Found: 323.1074.


F
F
O
Boc
MeO
159.18
158.43
155.51
153.27
152.59
129.44
129.40
129.37
123.61
123.58
123.54
114.07
89.30
89.13
89.11
88.95
82.54
63.09
63.06
63.03
63.01
55.23
27.72
f1 (ppm)

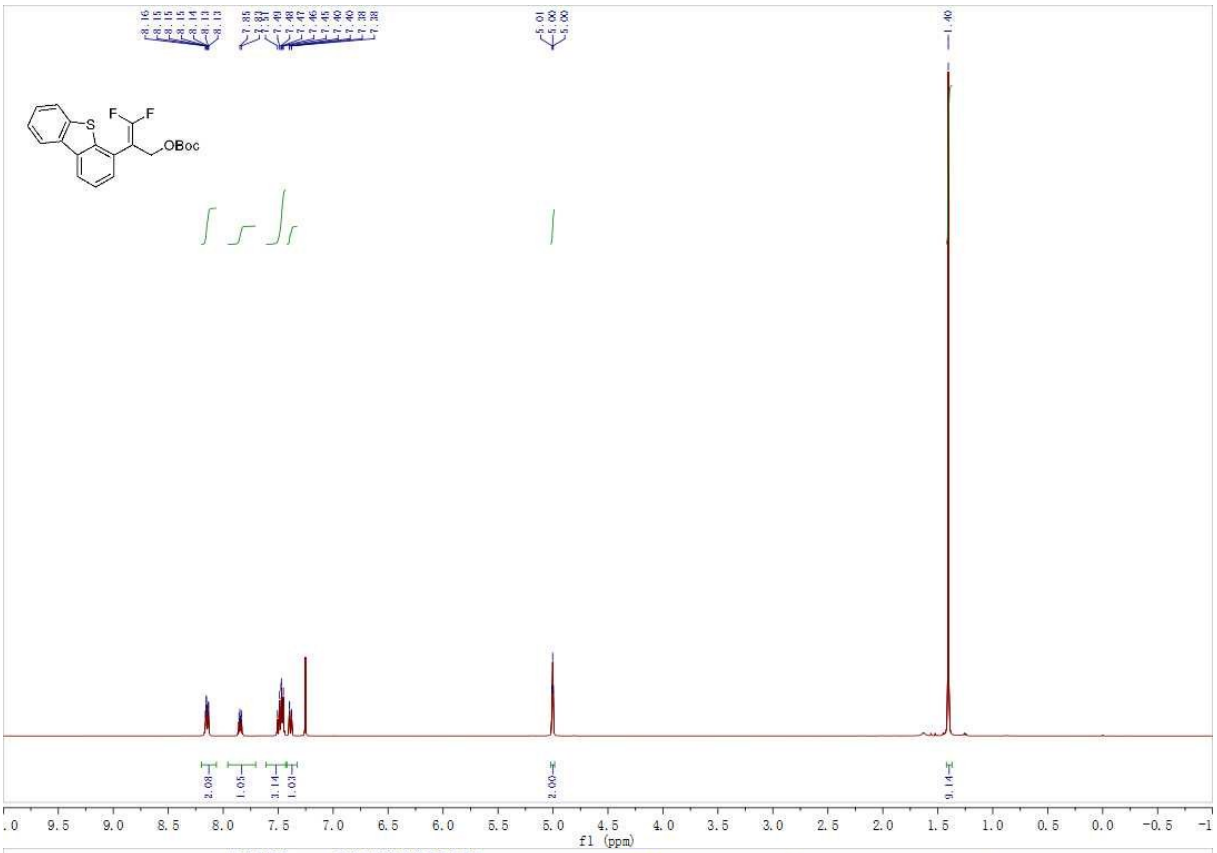

F
F
O
Boc
MeO
7.31
7.29
6.91
6.89
4.91
4.90
4.90
4.90
3.79
1.46
2.04
2.11
2.00
3.19
9.11
f1 (ppm)

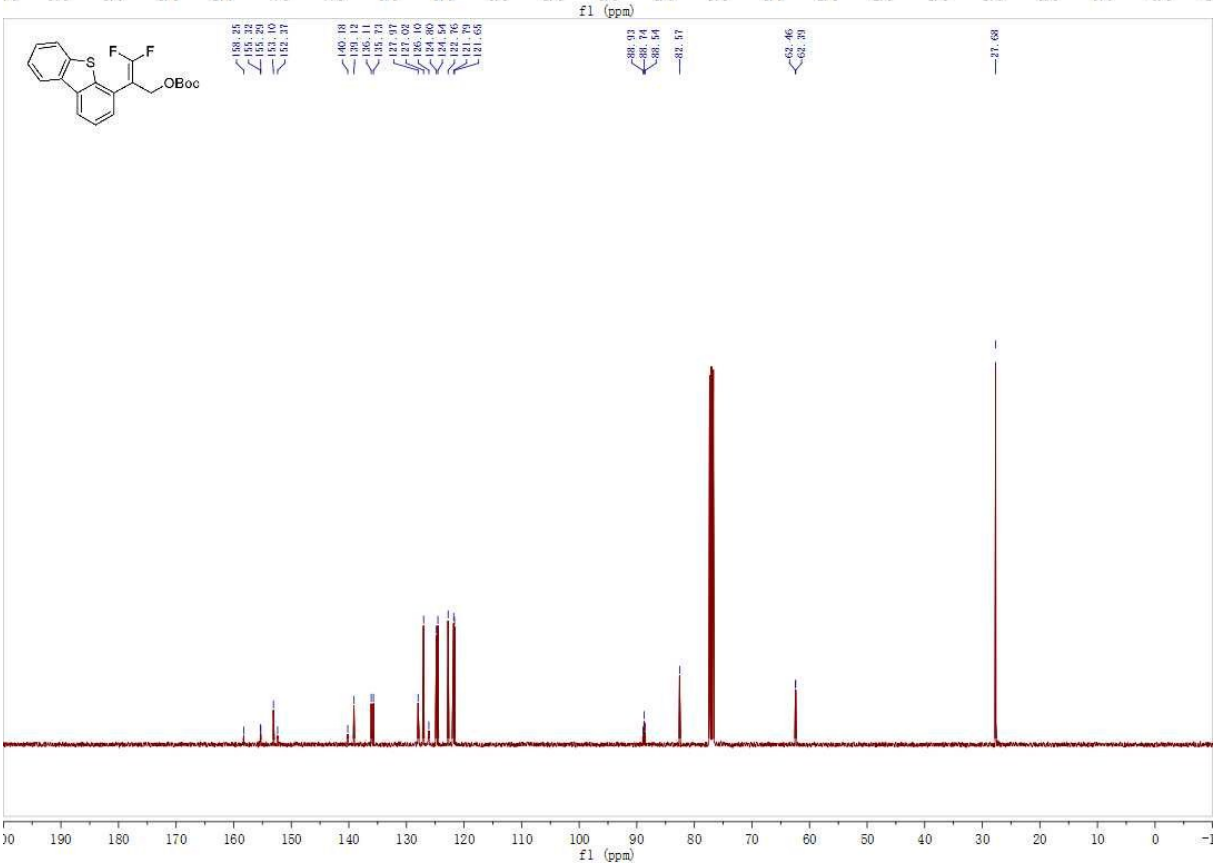


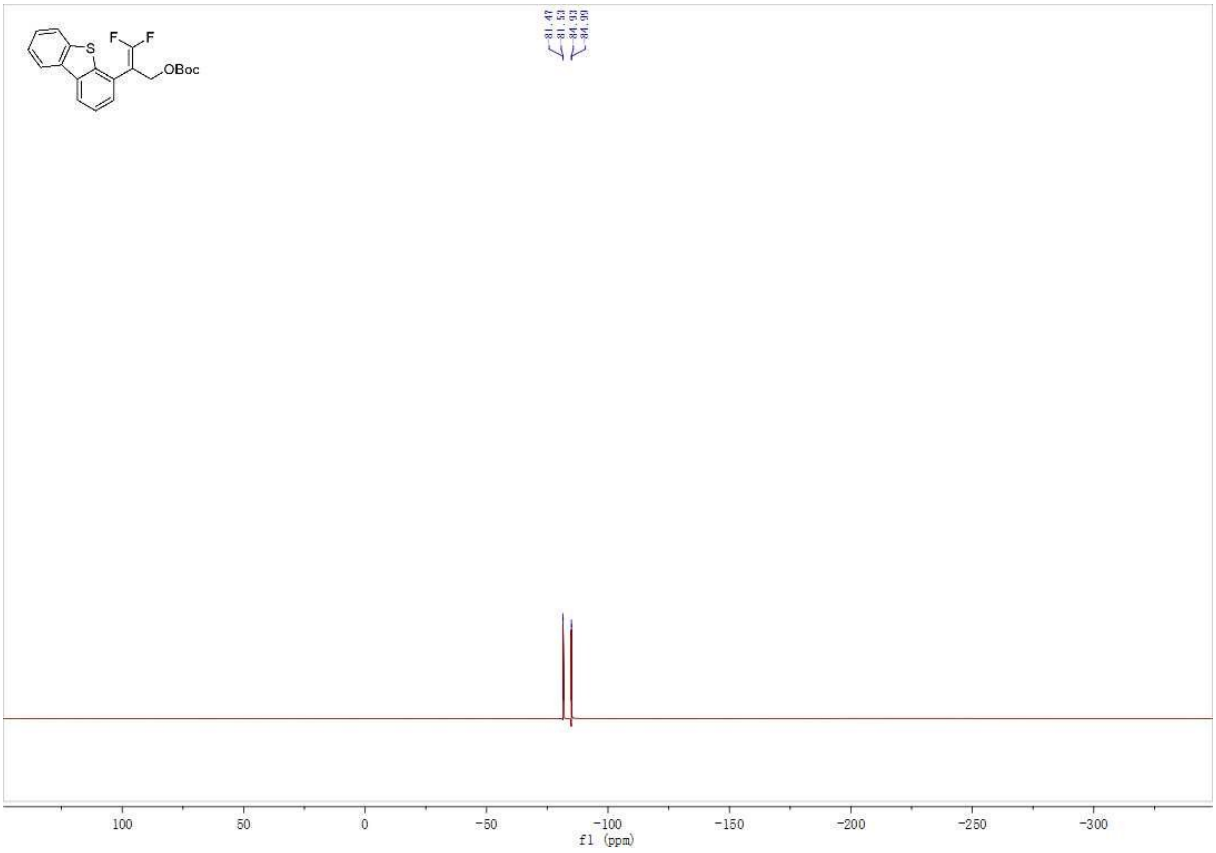
tert-butyl (2-(dibenzo[b,d]thiophen-4-yl)-3,3-difluoroallyl) carbonate (2e)



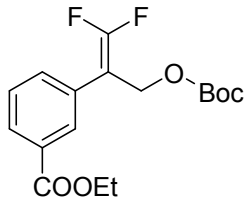
Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (50:1) as White solid (2.6 g, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 - 8.06 (m, 2H), 7.96 - 7.70 (m, 1H), 7.61 - 7.43 (m, 3H), 7.41 - 7.37 (m, 1H), 5.00 (s, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.31 (dd, *J* = 297.3, 294.2 Hz), 153.10, 140.18, 139.12, 136.11, 135.73, 127.97, 127.02, 126.10, 124.80, 124.54, 122.76, 121.79, 121.65 (s), 88.74 (dd, *J* = 19.19, 20.2Hz), 82.57, 62.43, 27.68. ^{19}F NMR (377 MHz, $CDCl_3$) δ -81.50 (d, *J* = 21.2 Hz), -84.96 (d, *J* = 21.2 Hz). HRMS (ESI^+): Calcd for $C_{20}H_{18}F_2O_3S$ $[Na]^+$: 399.0842, Found:399.0847.


F
F
S
OBoc
f1 (ppm)

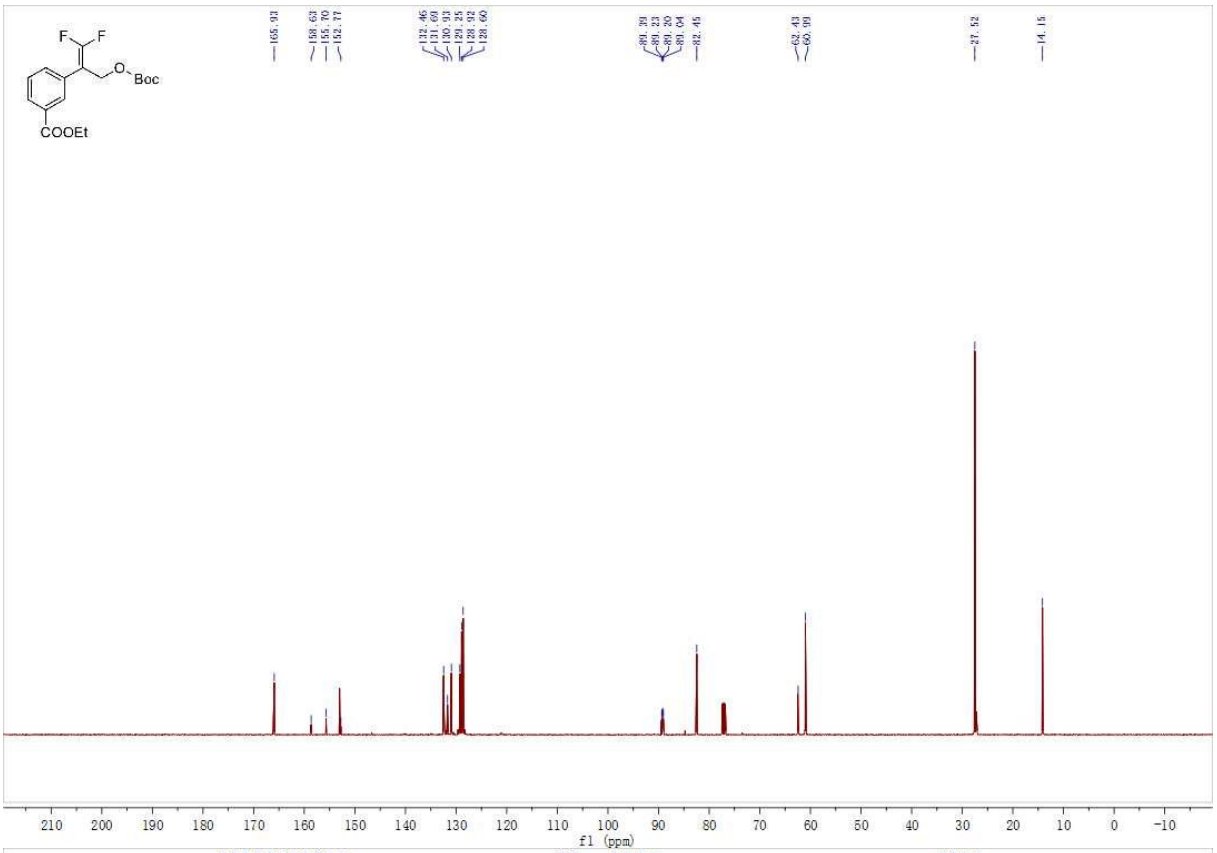

F
F
S
OBoc
f1 (ppm)

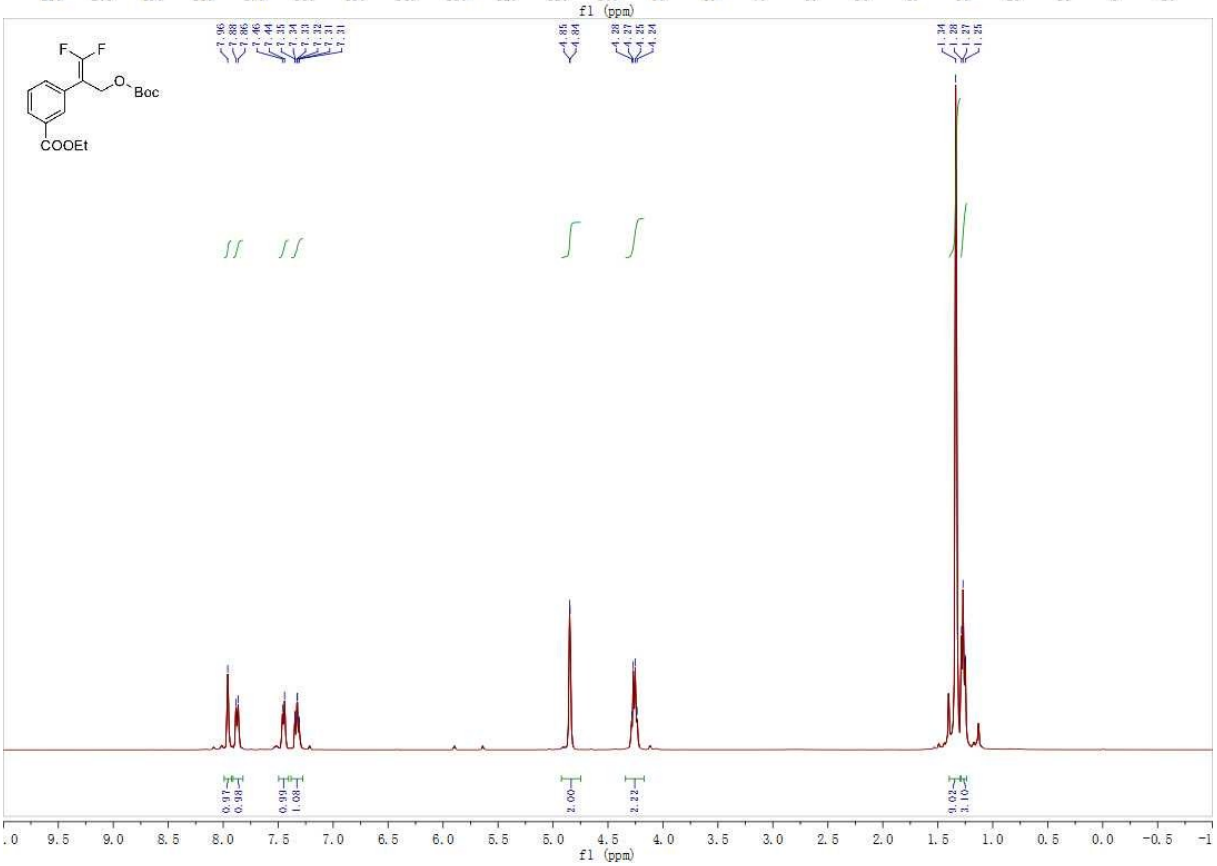


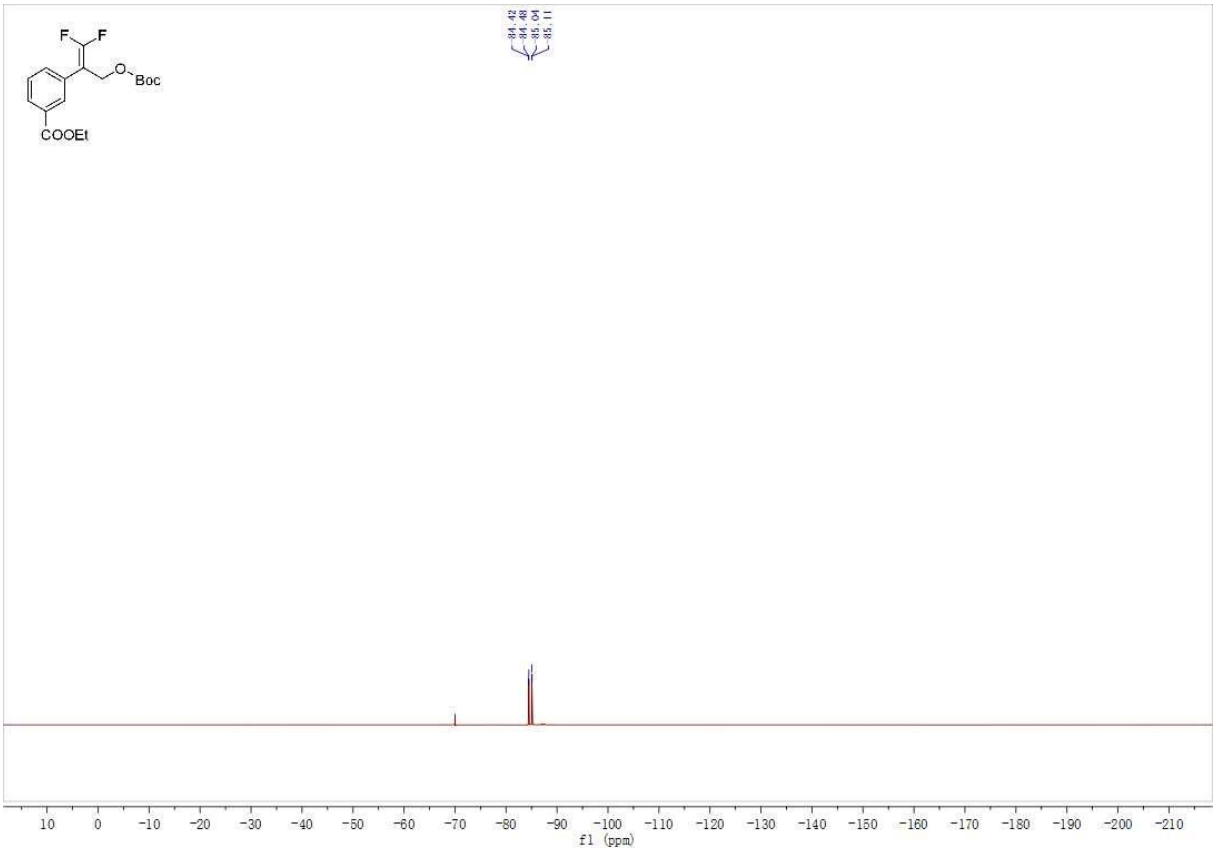
ethyl 3-(3-((tert-butoxycarbonyl)oxy)-1,1-difluoroprop-1-en-2-yl)benzoate (2f)



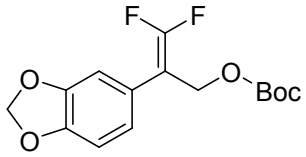
Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (30:1) as thick oil (2.3 g, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.36 - 7.29 (m, 1H), 4.85 (d, *J* = 1.7 Hz, 2H), 4.40 - 3.98 (m, 2H), 1.34 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.93, 155.70 (dd, *J* = 295.3 Hz), 153.02, 132.46, 131.69, 130.93, 129.25, 128.92, 128.60, 89.22 (dd, *J* = 19.2, 16.3 Hz), 82.45, 62.43, 60.99, 27.52, 14.15 . ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.45 (d, *J* = 24.5 Hz), -85.08 (d, *J* = 24.5 Hz). HRMS (ESI^+): Calcd for $C_{17}H_{20}F_2O_5$ $[H]^+$: 365.1176, Found: 365.1179.


F
F
O
Boc
COOEt
165.93
158.63
155.70
152.77
132.46
131.69
130.91
129.35
128.92
128.60
91.39
91.23
90.90
90.64
82.45
62.43
60.99
27.52
14.15
f1 (ppm)

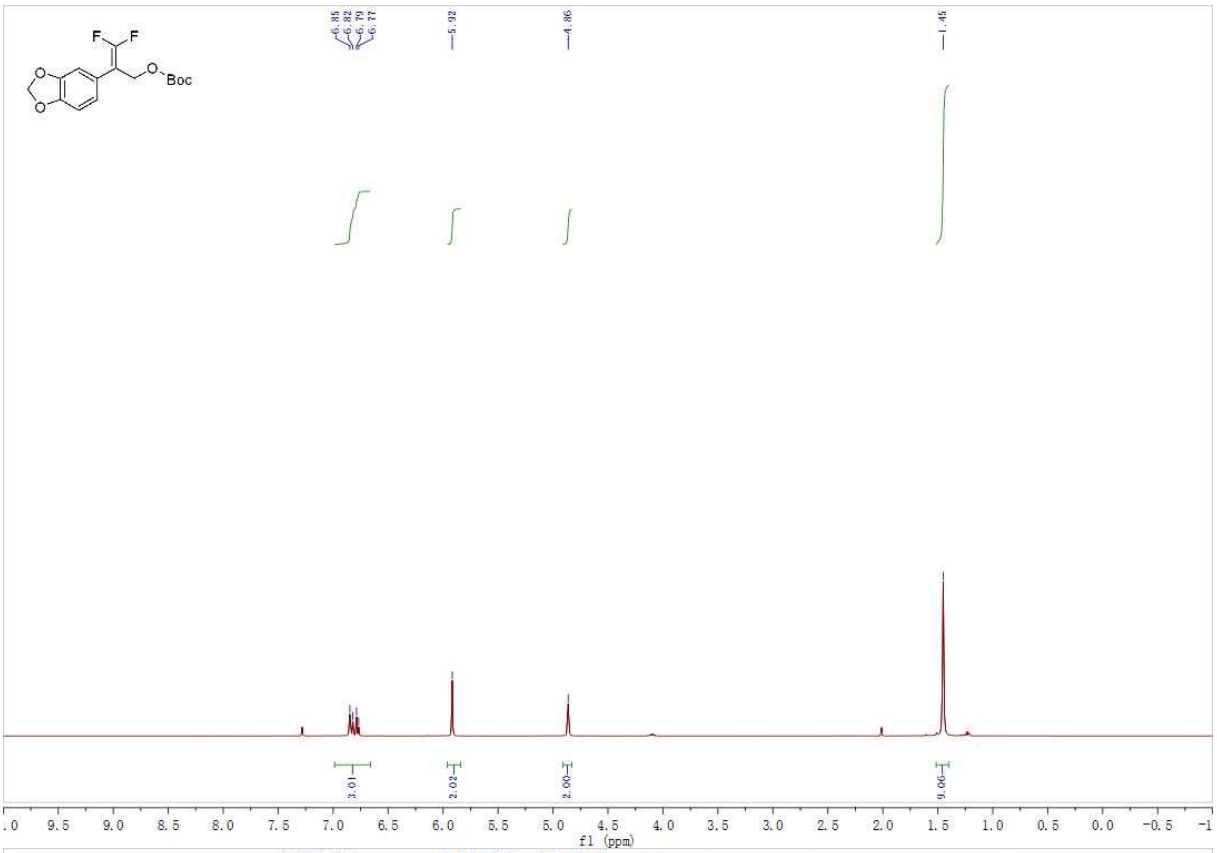

F
F
O
Boc
COOEt
7.96
7.88
7.86
7.46
7.44
7.35
7.34
7.33
7.32
7.31
7.31
4.85
4.84
4.38
4.37
4.35
4.34
1.34
1.28
1.27
1.26
0.97
0.98
0.99
1.08
2.00
2.23
9.02
3.10
f1 (ppm)



2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl tert-butyl carbonate (2g)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (50:1) as thick oil (2.3 g, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 - 6.69 (m, 3H), 5.92 (s, 2H), 4.86 (s, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.50 (dd, J = 294.92, 295.93 Hz), 153.13, 147.83, 147.24, 124.92, 121.87, 108.68, 108.33, 101.18, 89.40 (dd, J = 18.8, 16.9 Hz), 82.40, 62.94, 27.58. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.96 (d, J = 28.0 Hz), -86.09 (d, J = 28.0 Hz). HRMS (ESI^+): Calcd for $C_{15}H_{16}F_2O_5$ $[Na]^+$: 337.0863, Found: 337.0867.


F
F
O
O
Boc
6.85
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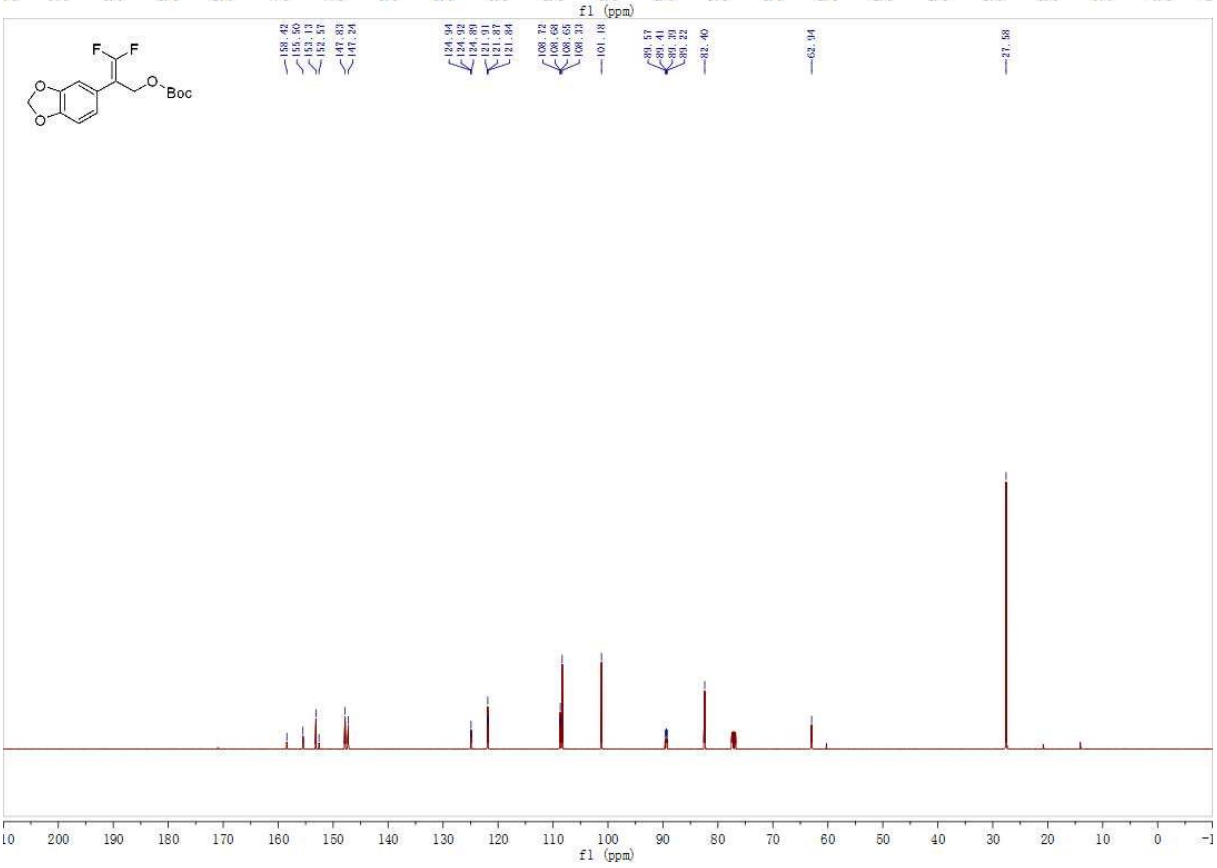
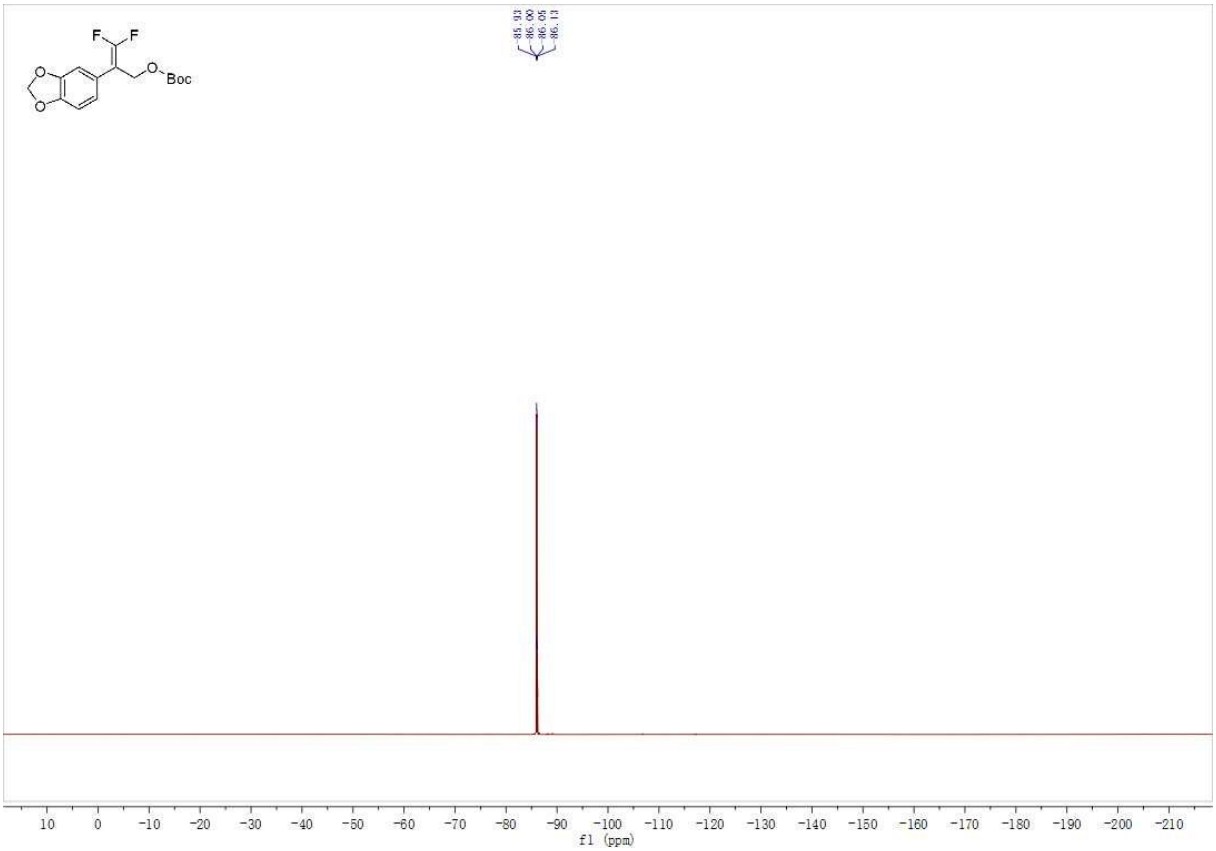
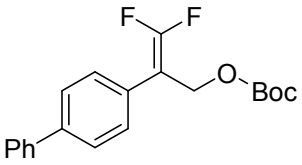
6.77
5.92
4.86
1.45
3.01
2.02
2.00
9.06
f1 (ppm)

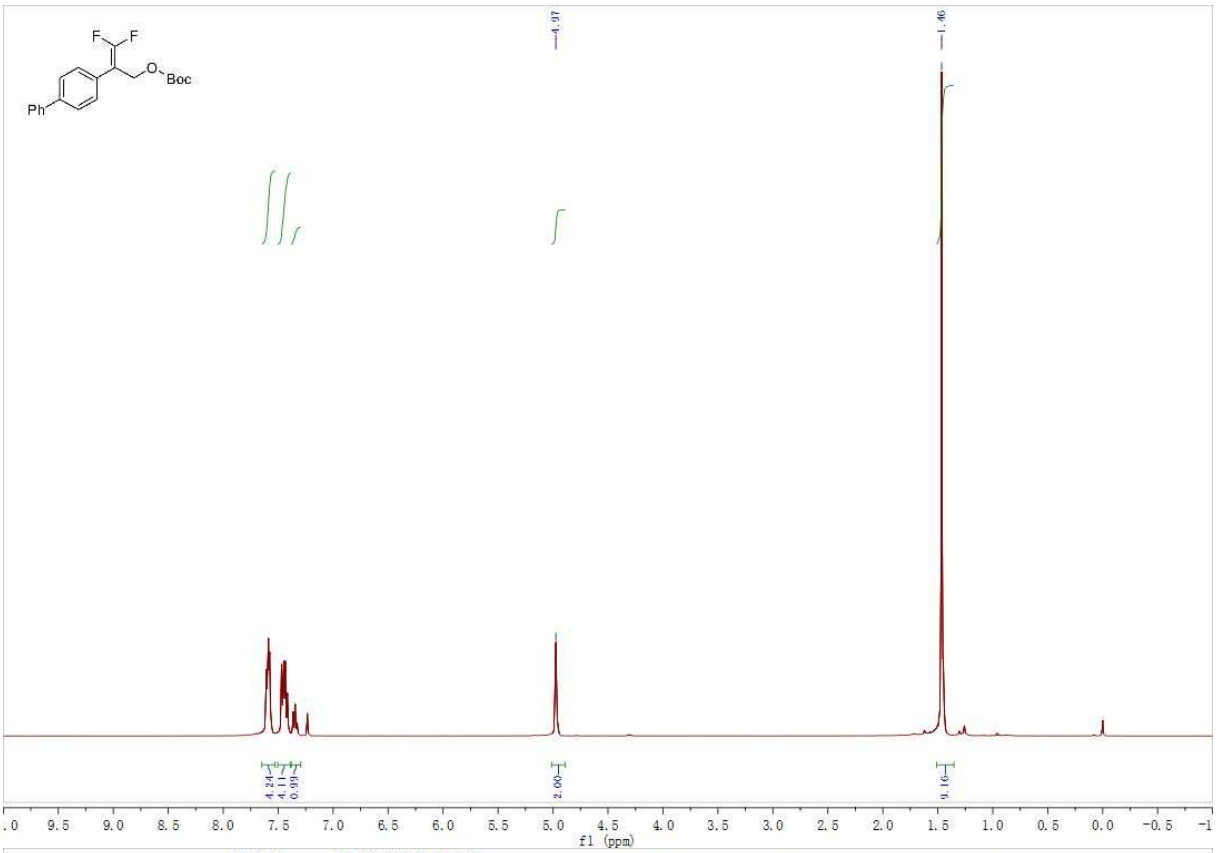

F
F
O
O
Boc
158.42
155.50
153.13
152.57
147.83
147.24
124.94
124.92
124.89
121.91
121.87
121.84
108.72
108.68
108.65
108.33
101.18
89.57
89.41
89.39
89.22
82.40
62.94
27.58
f1 (ppm)

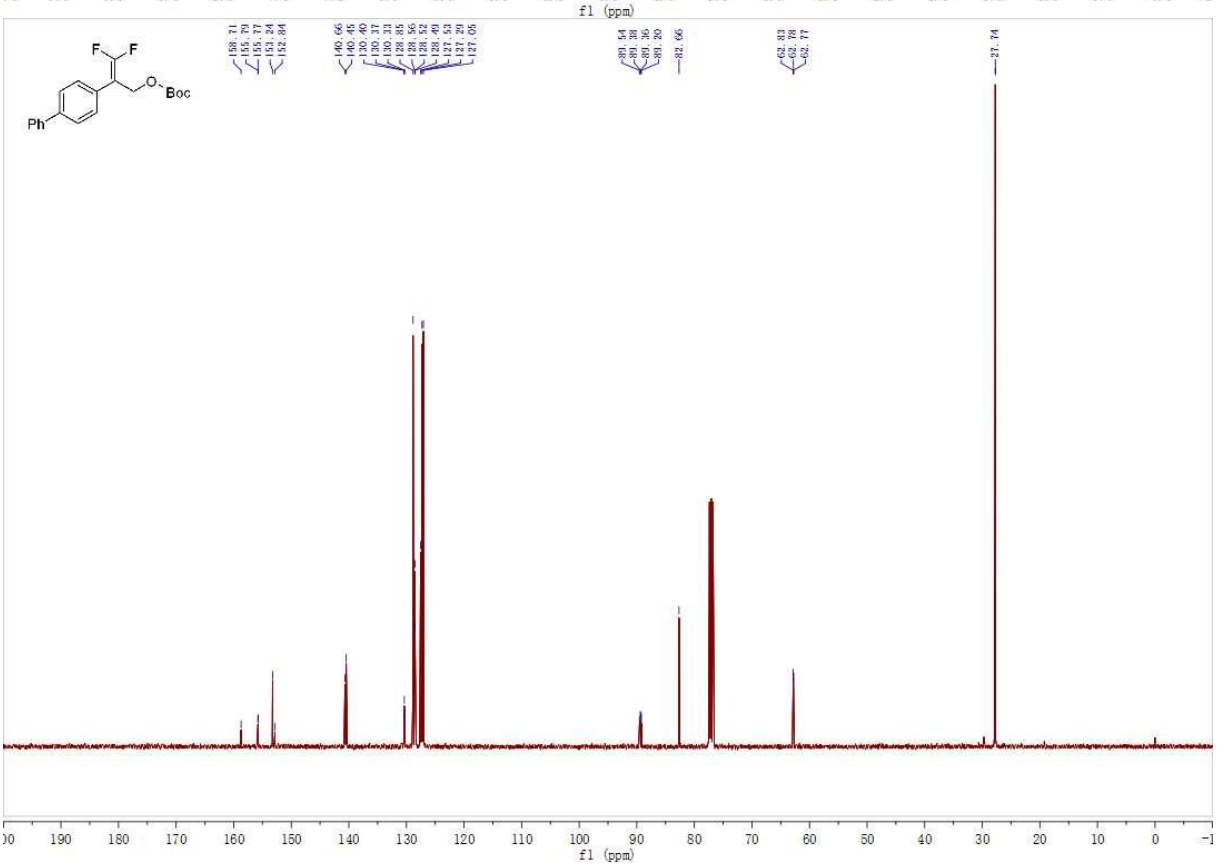


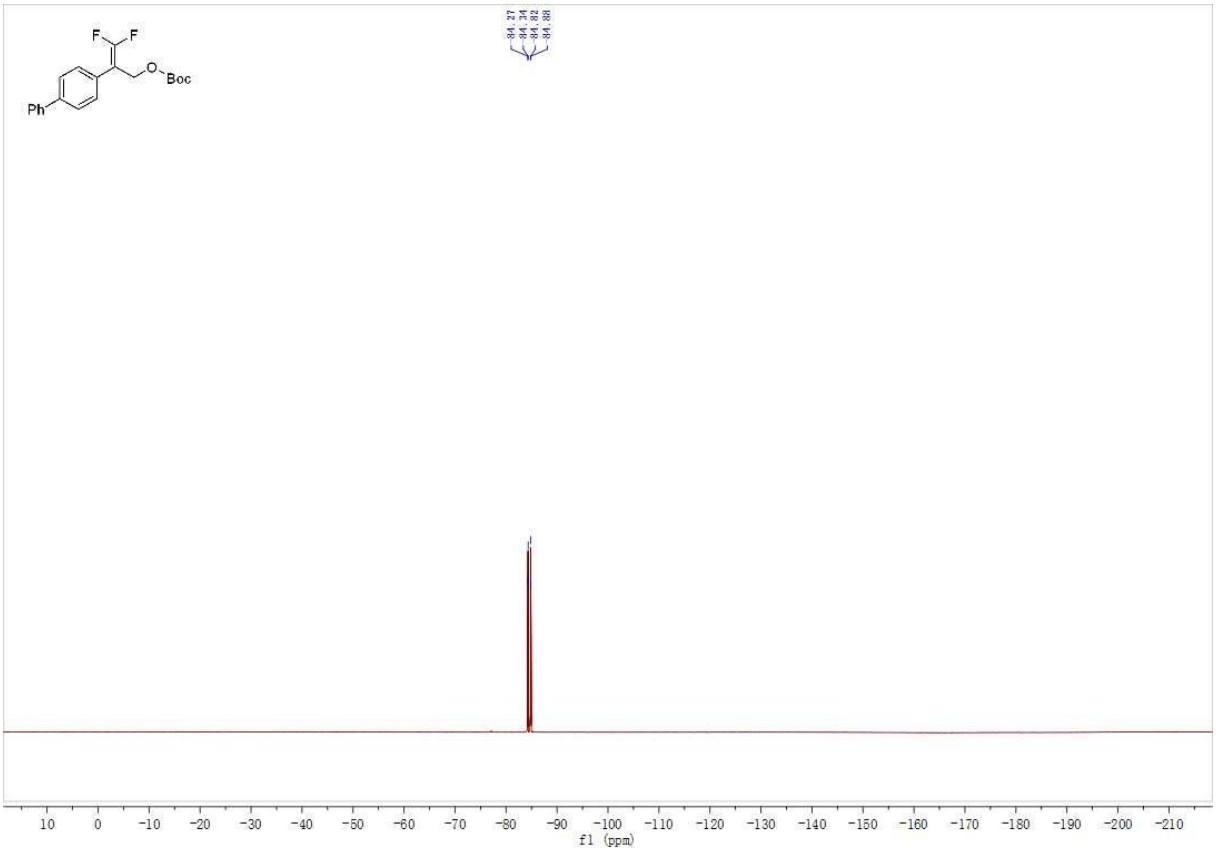
2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl tert-butyl carbonate (2h)



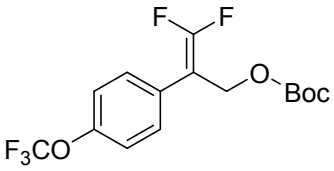
Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as white solid (2.6 g, 69 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 - 7.55 (m, 4H), 7. 50 - 7.40 (m, 4H), 7.38 - 7.31 (m, 1H), 4.97 (s, 2H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.78 (dd, *J* = 296.0, 294.7 Hz), 153.24, 140.66, 140.45, 130.37, 128.85, 128.52, 127.53, 127.29, 127.05, 89.37 (dd, *J* = 18.7, 16.1 Hz), 82.66, 62.78, 27.74. ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.30 (d, *J* = 25.0 Hz), -84.85 (d, *J* = 25.0 Hz). HRMS (ESI^+): Calcd for $C_{20}H_{20}F_2O_3$ $[Na]^+$: 369.1278, Found: 369.1256.


F
F
O
Boc
Ph
4.97
1.46
4.24
4.11
0.99
2.00
9.16
f1 (ppm)

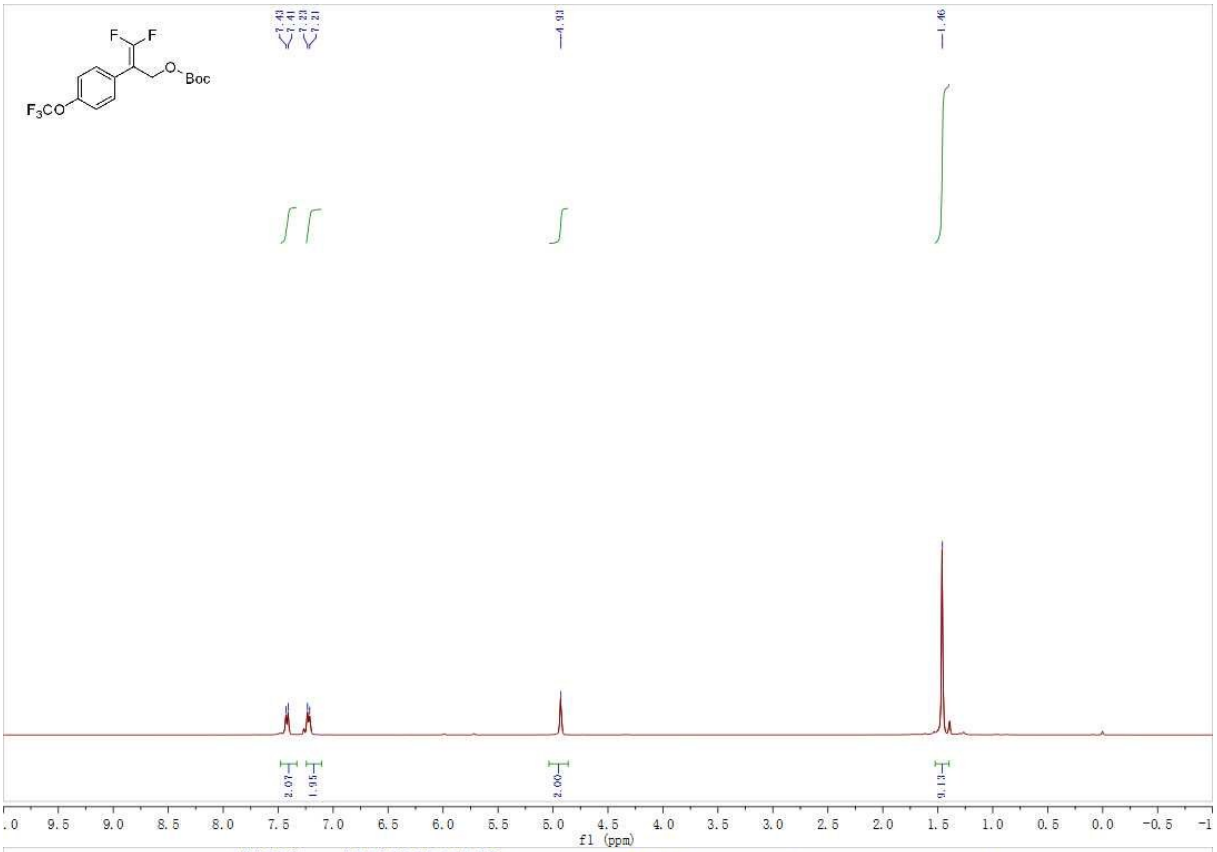

F
F
O
Boc
Ph
158.71
155.79
155.77
153.24
152.84
140.66
140.45
130.40
130.37
130.31
128.85
128.56
128.52
128.49
127.53
127.39
127.05
89.54
89.38
89.35
89.20
82.65
63.83
62.78
62.77
27.74
f1 (ppm)

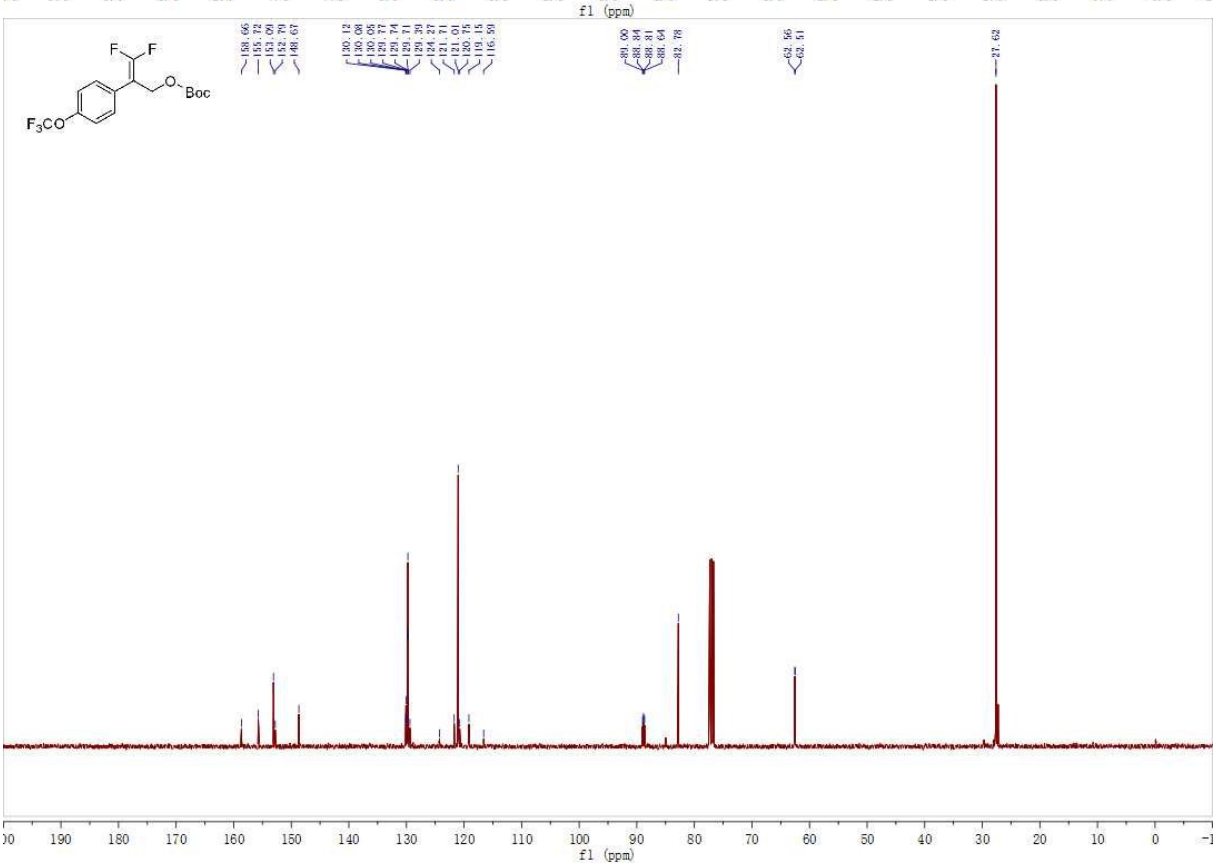


tert-butyl (3,3-difluoro-2-(4-(trifluoromethoxy)phenyl)allyl) carbonate (2i)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (2.3 g, 70 %).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.93 (s, 2H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.72 (dd, *J* = 296.94, 295.93 Hz), 153.09, 148.67 , 130.08, 129.74, 121.47 (q, 257.5 Hz), 121.01, 88.82 (dd, *J* = 19.5, 16.2 Hz), 82.78, 62.53 (d, *J* = 5.0 Hz), 27.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.93 (s), -84.12 (d, *J* = 24.2 Hz), -84.79 (d, *J* = 24.2 Hz). HRMS (ESI^+): Calcd for $C_{15}H_{15}F_5O_4$ $[Na]^+$: 377.0788, Found: 377.0796.


F
F
O
Boc
F3CO
7.43
7.41
7.23
7.21
4.93
1.46
2.07
1.95
2.00
9.13
f1 (ppm)


F
F
O
Boc
F3CO
158.66
155.72
153.09
152.79
148.67
120.12
120.08
120.05
129.77
129.74
129.71
129.39
124.37
121.71
121.01
120.75
119.15
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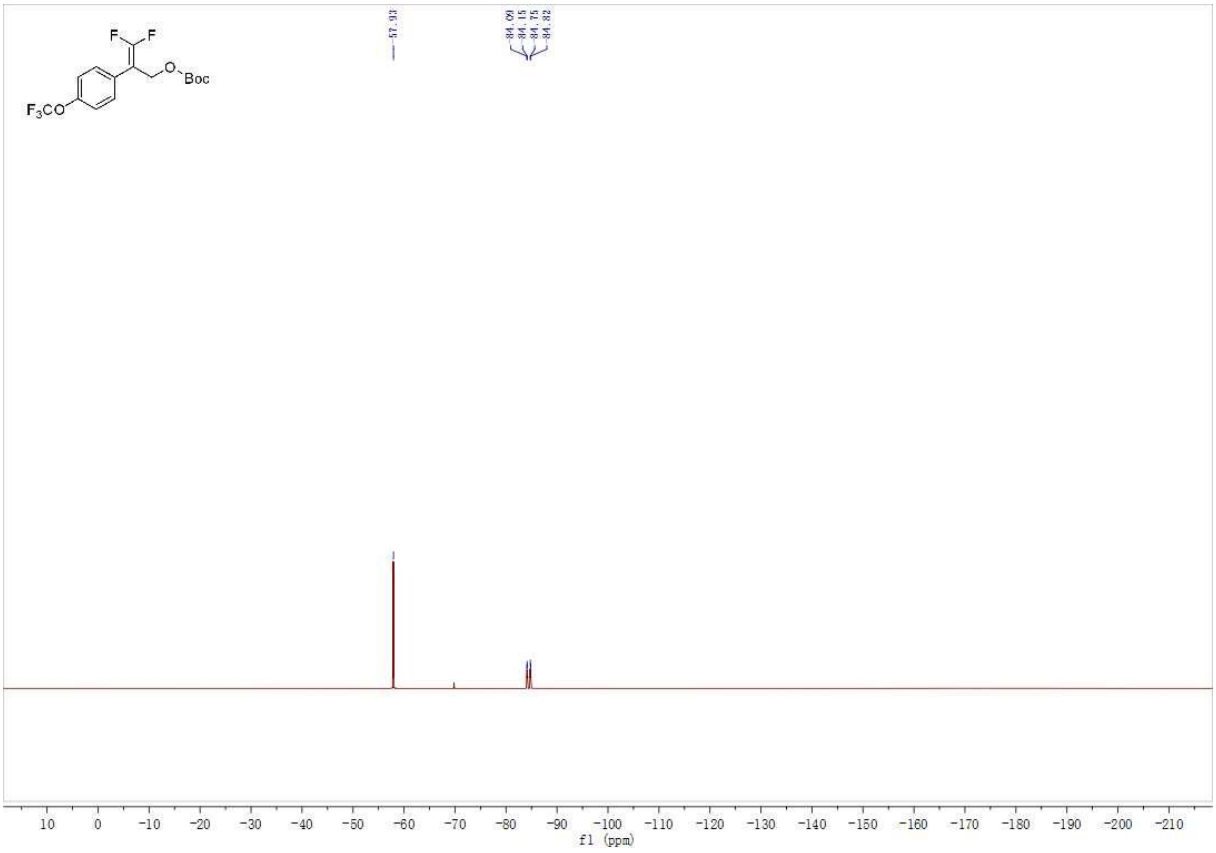
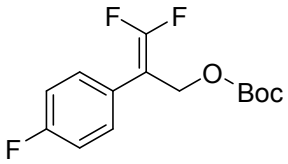
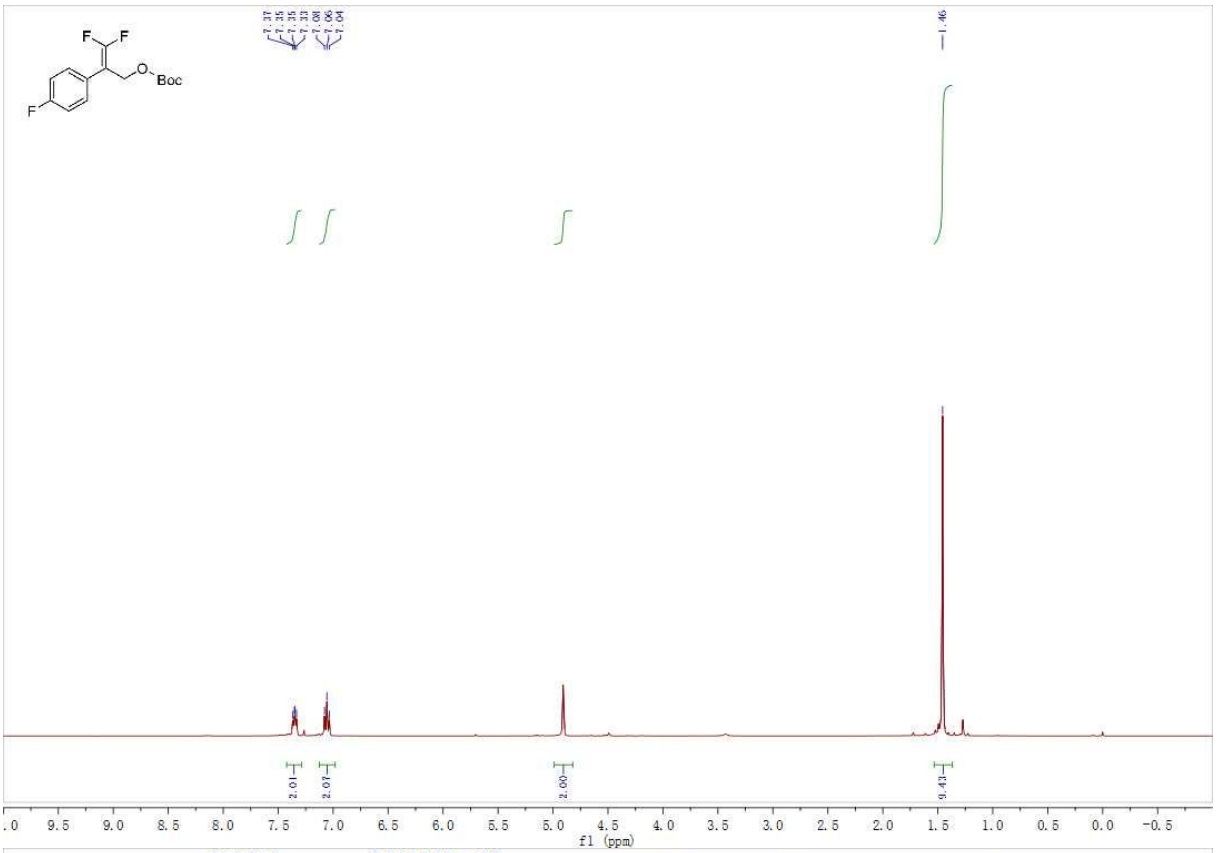
80.00
88.84
88.81
88.64
82.78
62.55
62.51
27.62
f1 (ppm)

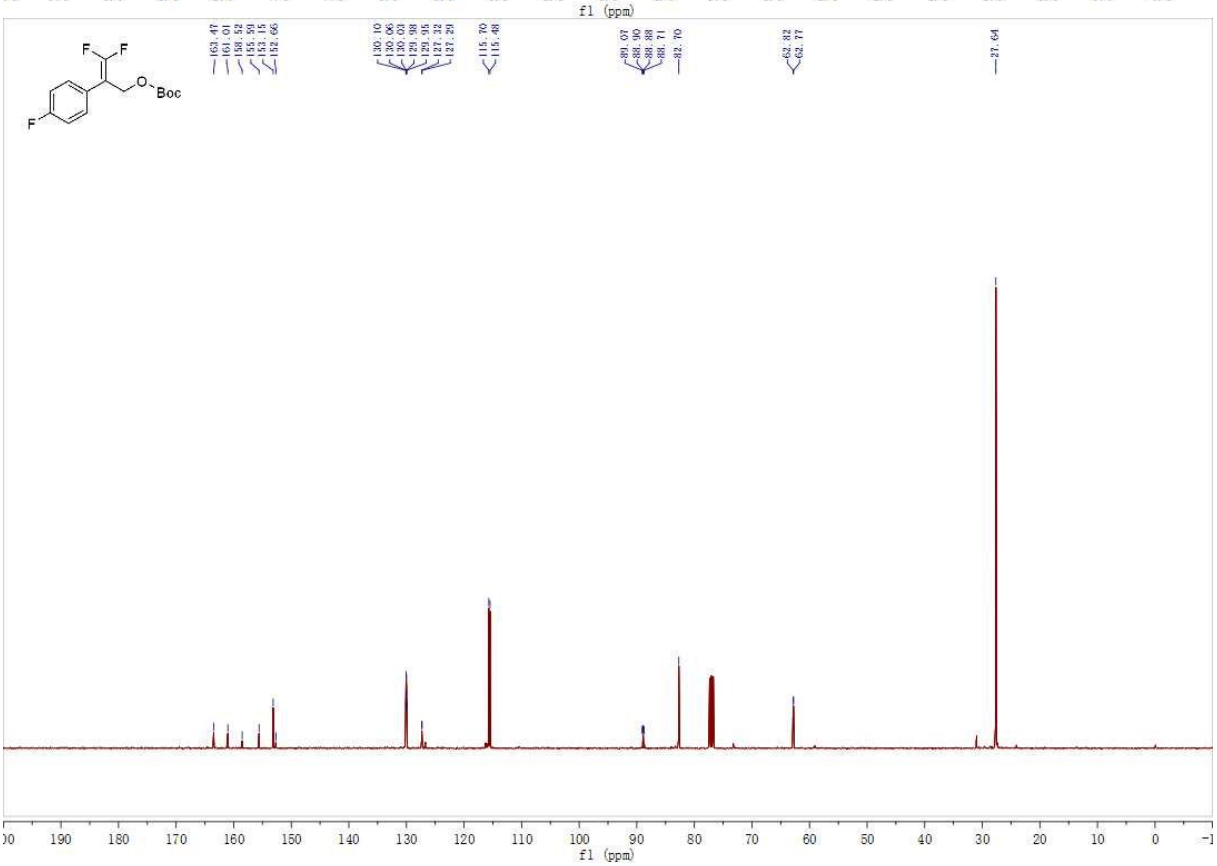


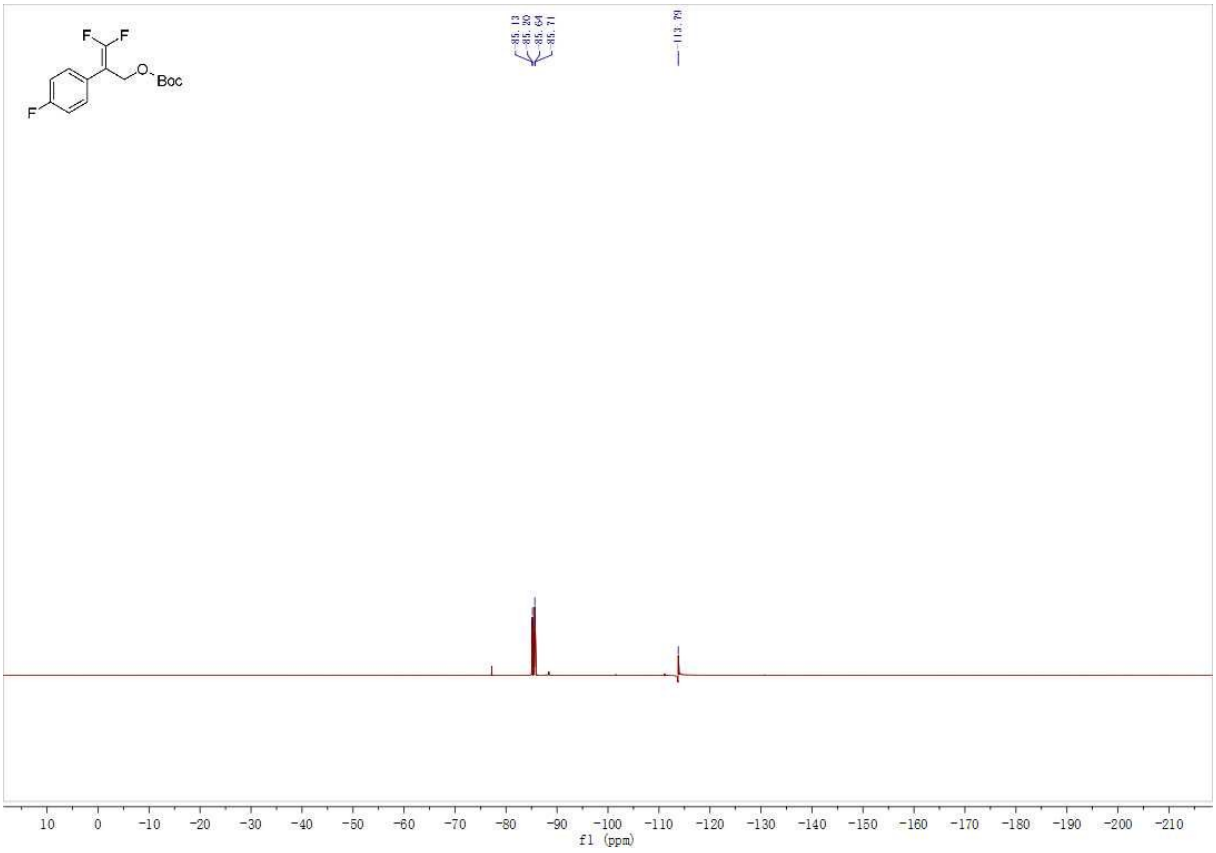
tert-butyl (3,3-difluoro-2-(4-fluorophenyl)allyl) carbonate (2j)



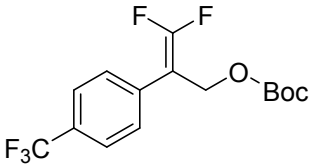
Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (1.9 g, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.32 (m, 2H), 7.10 - 7.02 (m, 2H), 4.91 (s, 2H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.24 (d, J = 247.6 Hz), 155.59 (dd, J = 295.93, 294.93 Hz), 153.15, 130.03, 127.32, 115.59 (d, J = 21.7 Hz), 88.89 (dd, J = 19.2, 16.6 Hz), 82.70, 62.77, 27.64. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.16 (d, J = 26.4 Hz), -85.68 (d, J = 26.4 Hz), -113.79 (s). HRMS (ESI^+): Calcd for $C_{14}H_{15}F_3O_3$ $[Na]^+$: 311.0871, Found: 311.0876.


F
F
O
Boc
F
7.37
7.35
7.33
7.08
7.06
7.04
1.46
2.01
2.07
2.00
9.43
f1 (ppm)

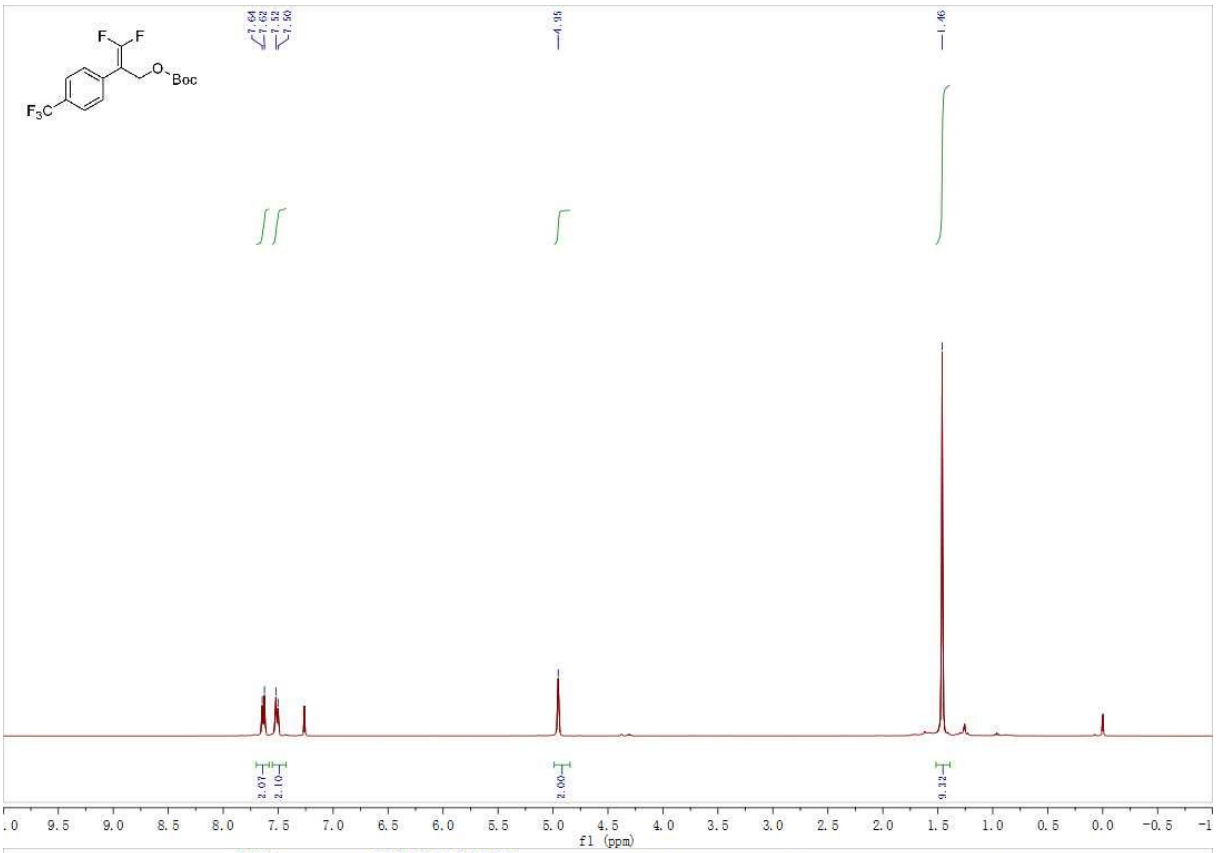

F
F
O
Boc
F
163.47
161.01
158.52
155.99
153.15
152.66
130.10
130.06
130.03
129.98
129.95
127.32
127.29
115.70
115.48
81.07
80.90
80.88
80.71
62.82
62.77
27.64
f1 (ppm)

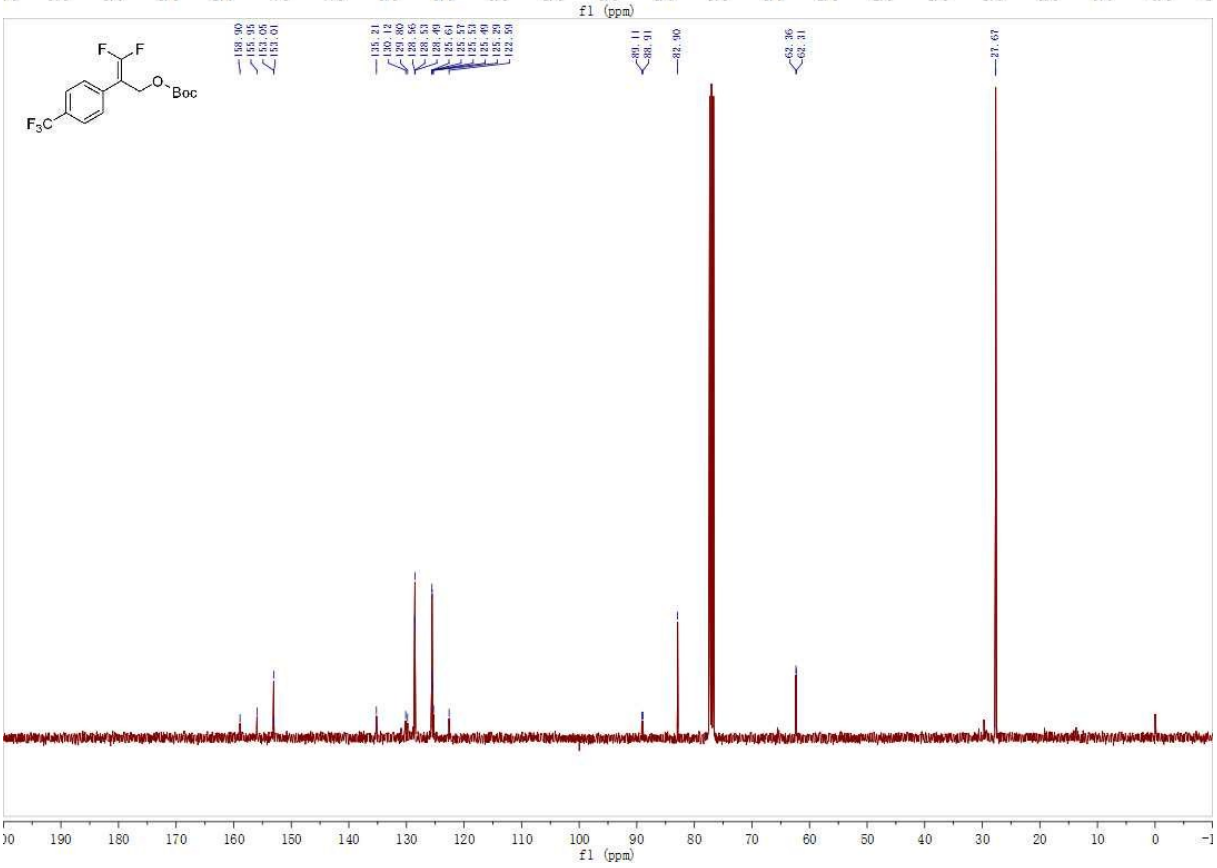


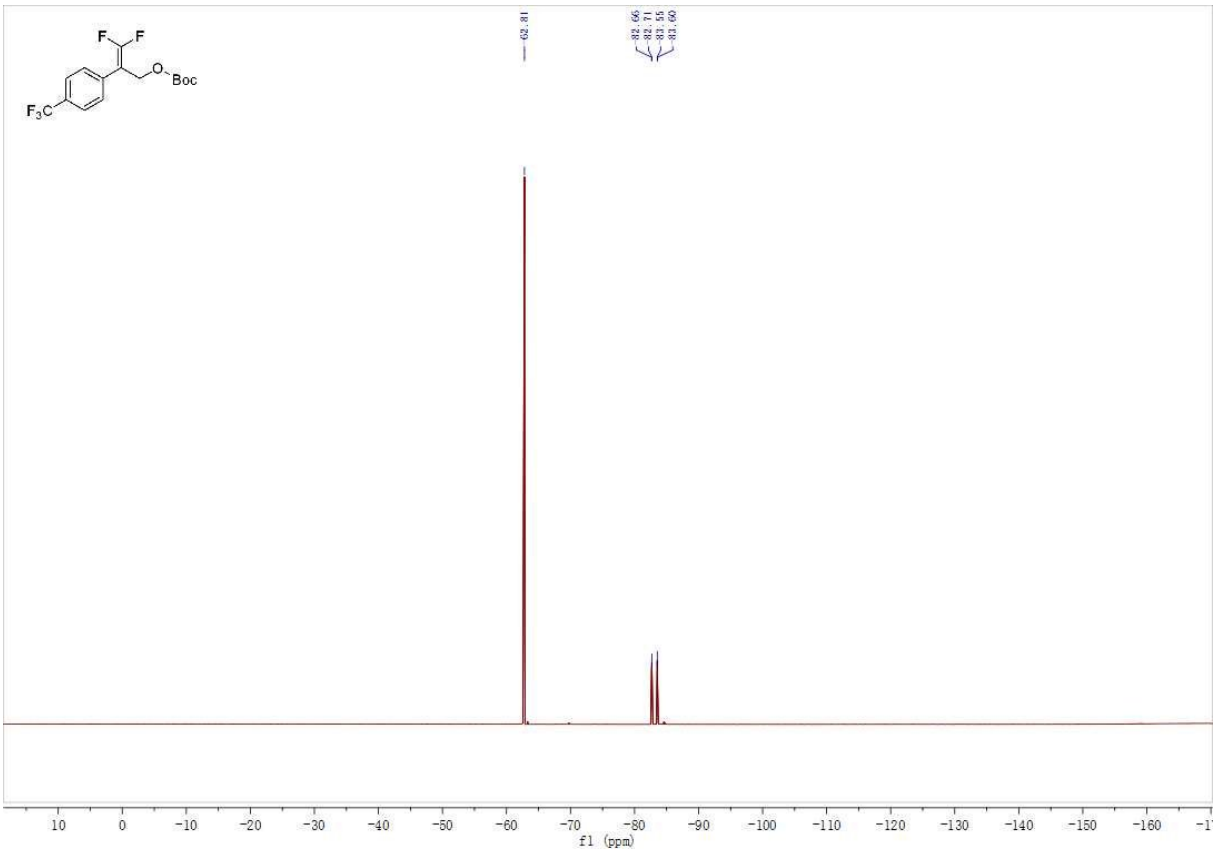
tert-butyl (3,3-difluoro-2-(4-(trifluoromethyl)phenyl)allyl) carbonate (2k)



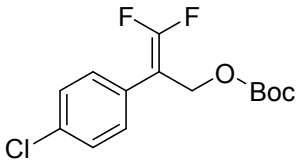
Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (2.3 g, 64 %).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 4.95 (s, 2H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.95 (dd, *J* = 292.1, 288.3 Hz), 153.05, 135.21, 130.34 (q, *J* = 129.98 Hz), 128.53, 125.57, 122.59 , 89.09 (dd, *J* = 19.6, 15.7 Hz), 82.90, 62.31, 27.67. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.81 (s), -82.69 (d, *J* = 21.4 Hz), -83.57 (d, *J* = 21.4 Hz). HRMS (ESI^+): Calcd for $C_{15}H_{15}F_5O_3$ $[Na]^+$: 361.0839, Found: 361.0842.


F
F
O
Boc
F3C
7.64
7.62
7.52
7.50
4.95
1.46
2.07
2.10
2.00
9.32
f1 (ppm)

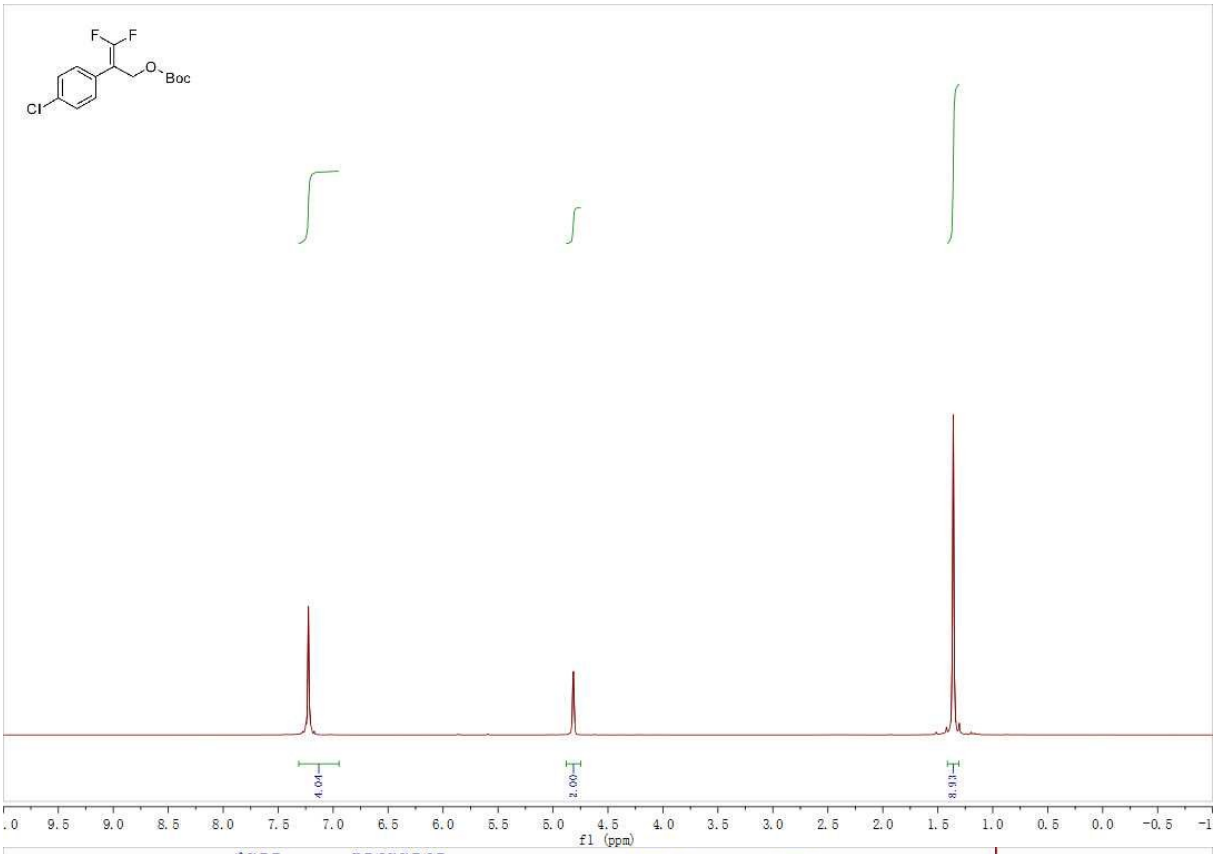

F
F
O
Boc
F3C
158.90
155.96
153.56
153.01
135.21
130.12
129.80
128.56
128.53
128.49
125.61
125.57
125.53
125.49
125.29
122.59
80.11
80.91
62.36
62.31
27.67
f1 (ppm)

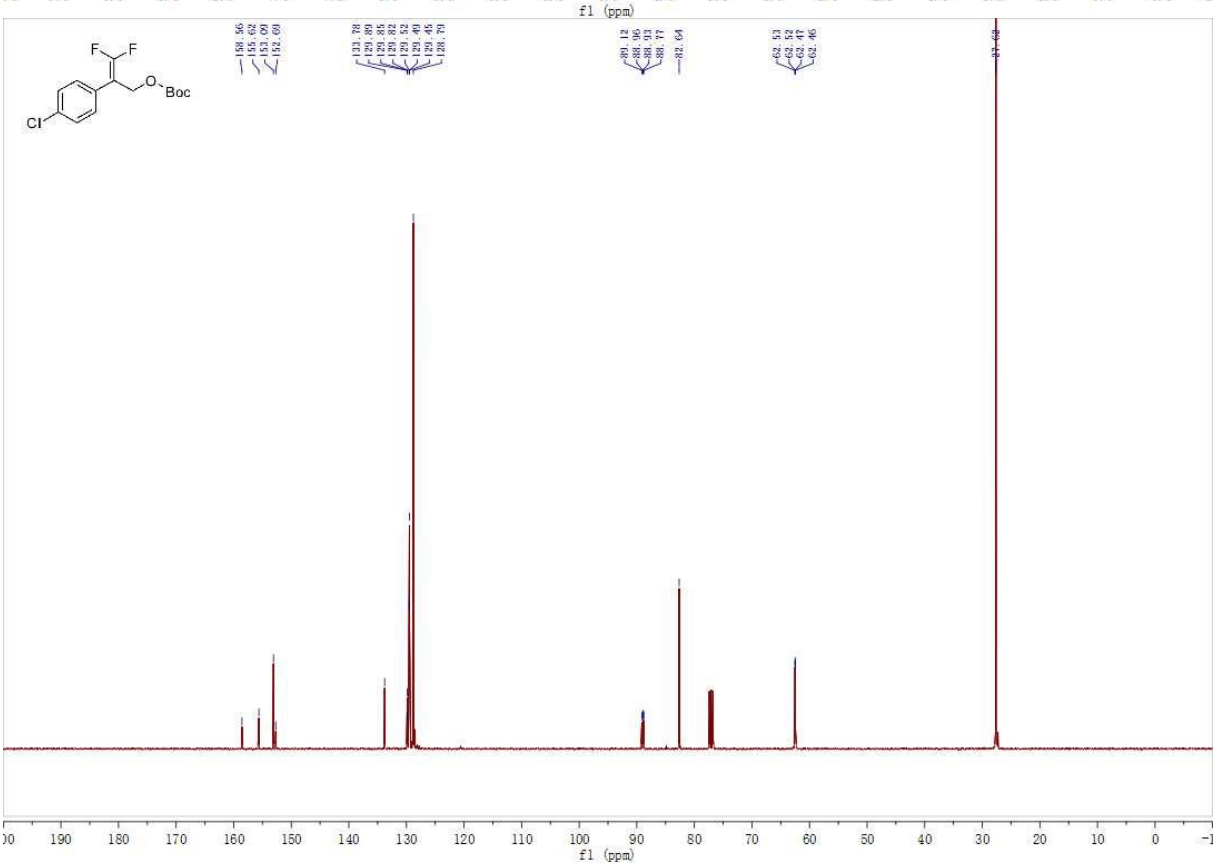


tert-butyl (2-(4-chlorophenyl)-3,3-difluoroallyl) carbonate (2l)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (2.2 g, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 4H), 4.81 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.62 (dd, J = 296.94, 295.93 Hz), 153.09, 133.78, 129.85, 129.49, 128.79, 88.94 (dd, J = 19.3, 16.1 Hz), 82.64, 62.52, 27.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.20 (d, J = 24.5 Hz), -84.80 (d, J = 24.5 Hz). HRMS (ESI^+): Calcd for $C_{14}H_{15}ClF_2O_3$ $[Na]^+$: 327.0575, Found: 327.0593.


F
F
O
Boc
Cl
4.04
2.00
8.93
f1 (ppm)


F
F
O
Boc
Cl
158.56
155.62
153.09
152.60
133.78
129.89
129.85
129.82
129.32
129.40
129.45
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80.96
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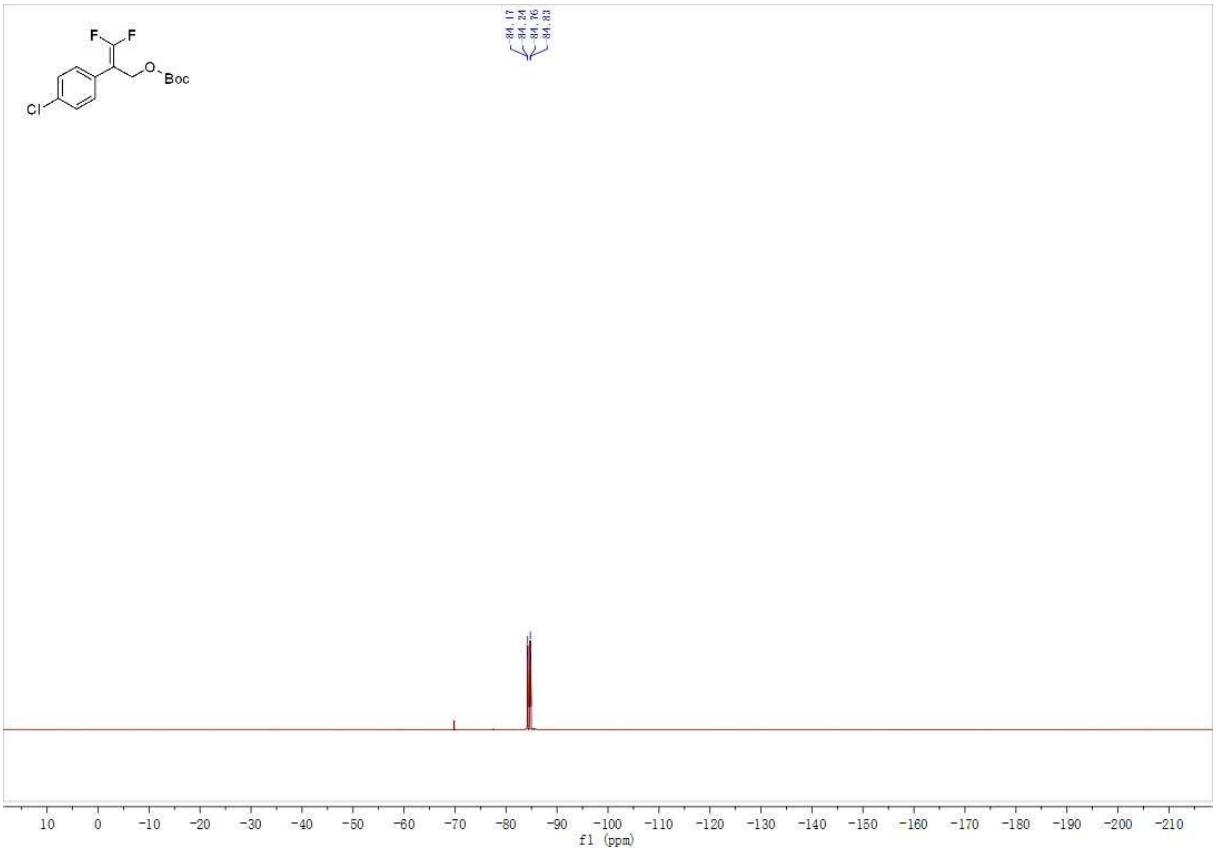
80.77
62.53
62.52
62.47
62.46
27.64
f1 (ppm)



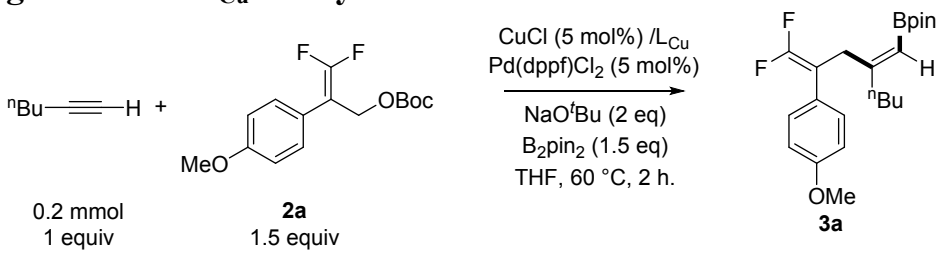
3. General Experimental Procedures

3.1 Screening of reaction conditions

In an Ar-filled dry box, Copper source (5 mol%, 0.01 mmol) and lignad were added to a 10 mL Schlenk tube containing a magnetic stirring bar. Then 1 mL dry solvent were added to the mixture, the Schlenk tube was sealed and removed from the dry box and stirred during 15 minutes at r.t. Then B_2pin_2 (1.5 eq, 0.3 mmol) and base (2.0 equiv, 0.4 mmol) were added to the mixture to afford a black suspension. In a separate vial Palladium source (5 mol%, 0.01 mmol), ligand (5 mol%, 0.01 mmol) and 2**a** (1.5 equiv, 0.3 mmol) were stirred in dry solvent (1 mL) for 15 minutes at r.t. **1a** (1 equiv, 0.2 mmol) and this solution and was finally added to the Schlenk tube and heated at 60 ºC for 2h. After this time, then reaction was cooled to room temperature. Et_2O and water were added and the layers were separated. The aqueous phase was extracted with Et_2O (x 2) and the combined organic layers were dried over Na_2SO_4 and concentrated. The

residue was purified by flash column chromatography on silica gel to give **3a**. The yield and regioselectivity was determined by GC with benzophenone as internal standard.

Screening of the Cu-L_{Cu} catalyst seffect on the reactions



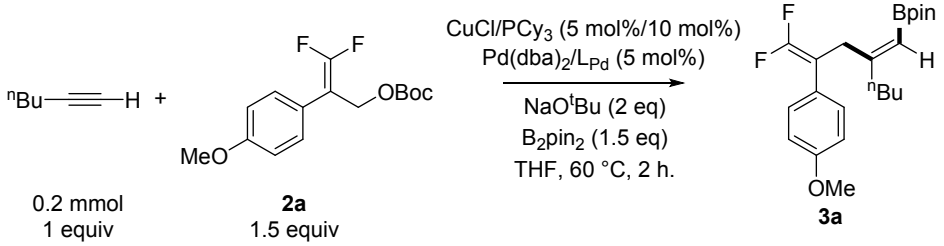
0.2 mmol
1 equiv

2a
1.5 equiv

3a

Entry	Cu-L_{Cu}	NMR Yield(%)
1	Dppf （5 mol%）	58
2	Xantphos (5 mol%)	trace
3	Cy-xantphos (5 mol%)	22
4	IMes·HCl (5 mol%)	trace
5	**PCy_3 (**10 mol%**)**	**84**
6	P^tBu_3 (10 mol%)	28
7	PPh_3 (10 mol%)	40
8	/	none

Screening of the Pd-L_{Pd} catalyst seffect on the reactions



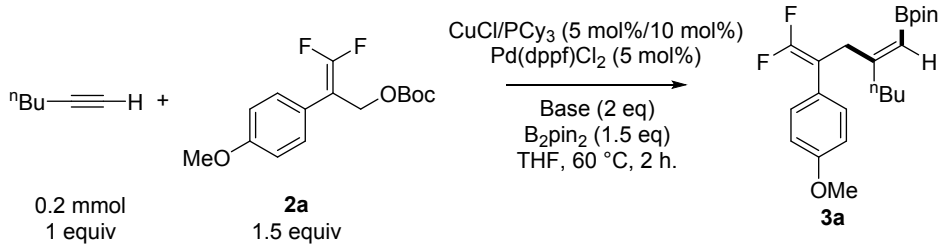
0.2 mmol
1 equiv

2a
1.5 equiv

3a

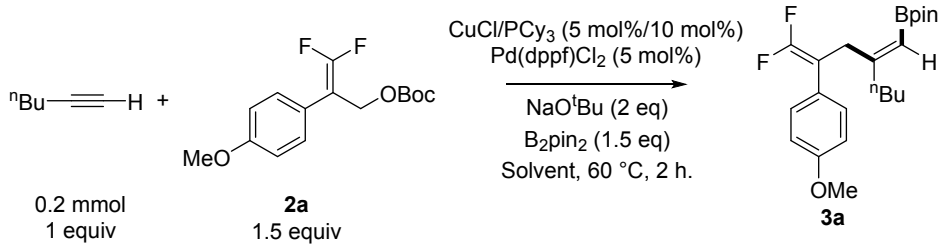
Entry	Pd-L_{Pd}	NMR Yield(%)
9	**Dppf** （5 mol%）	**81**
10	Dppe （5 mol%）	trace
11	IMes·HCl （5 mol%）	63
12	PPh_3 （10mol%）	48
13	/	none

Screening of the Base effect on the reactions



Entry	Base	NMR Yield(%)
14	CH_3ONa	70
15	**NaO^{t}Bu**	**84**
16	KO^{t}Bu	44
17	LiO^{t}Bu	24
18	K_2CO_3	none
19	LiOTMS	trace

Screening of the Solvent effect on the reactions

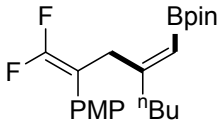


Entry	Solvent	NMR Yield(%)
18	Dioxane	57
19	**THF**	**84**
20	toluene	36
21	DCM	21

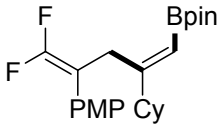
3.2 General Procedure for the Boryldifluoroallylation of Alkynes

In an Ar-filled dry box, CuCl (5 mol%, 1 mg) and tricyclohexylphosphine (10 mol%, 5.6 mg) were added to a 5 mL Schlenk tube containing a magnetic stirring bar. Then the dry THF (1 mL) were added to the mixture, the Schlenk tube was sealed and removed from the dry box and stirred during 15 minutes at r.t. Then B_2pin_2 (1.5 eq, 0.3 mmol, 76mg) and NaO^{t}Bu (2.0 equiv, 0.4 mmol, 38.4 mg) were added to the mixture to afford a black suspension. In a separate vial Pd(dppf)Cl_2 (5 mol%, 0.001 mmol, 7.1 mg) and tert-butyl (3,3-difluoro-2-

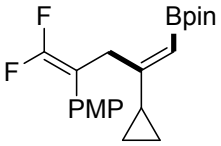
(4-methoxyphenyl)allyl) carbonate **2a** (1.5 equiv, 0.3 mmol, 90 mg) were stirred in dry THF (1 mL) for 15 minutes at r.t. The hex-1-yne **1a** (1 equiv, 0.2 mmol, 16 mg) and this solution and was finally added to the Schlenk tube and heated at 60 ^{o}C for 2h. After this time, then reaction was cooled to room temperature. Et_2O and water were added and the layers were separated. The aqueous phase was extracted with Et_2O (x 2) and the combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel to give **3a**.



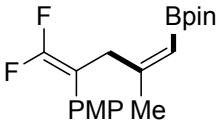
3a



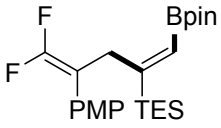
3b



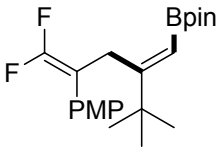
3c



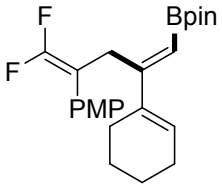
3d



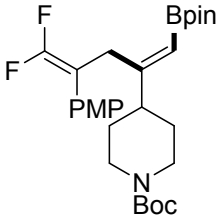
3e



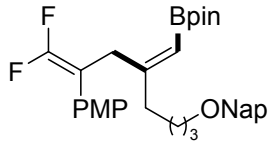
3f



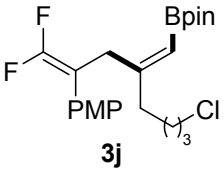
3g



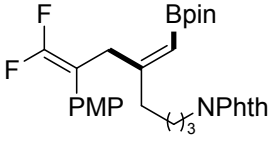
3h



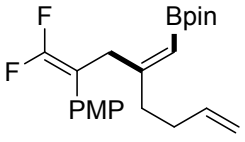
3i



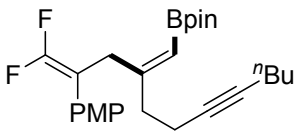
3j



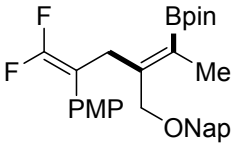
3k



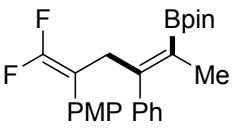
3l



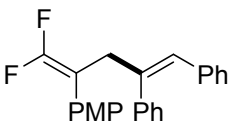
3m



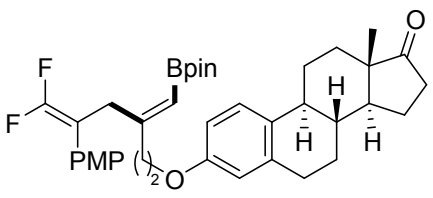
3n



3o

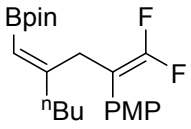


3p

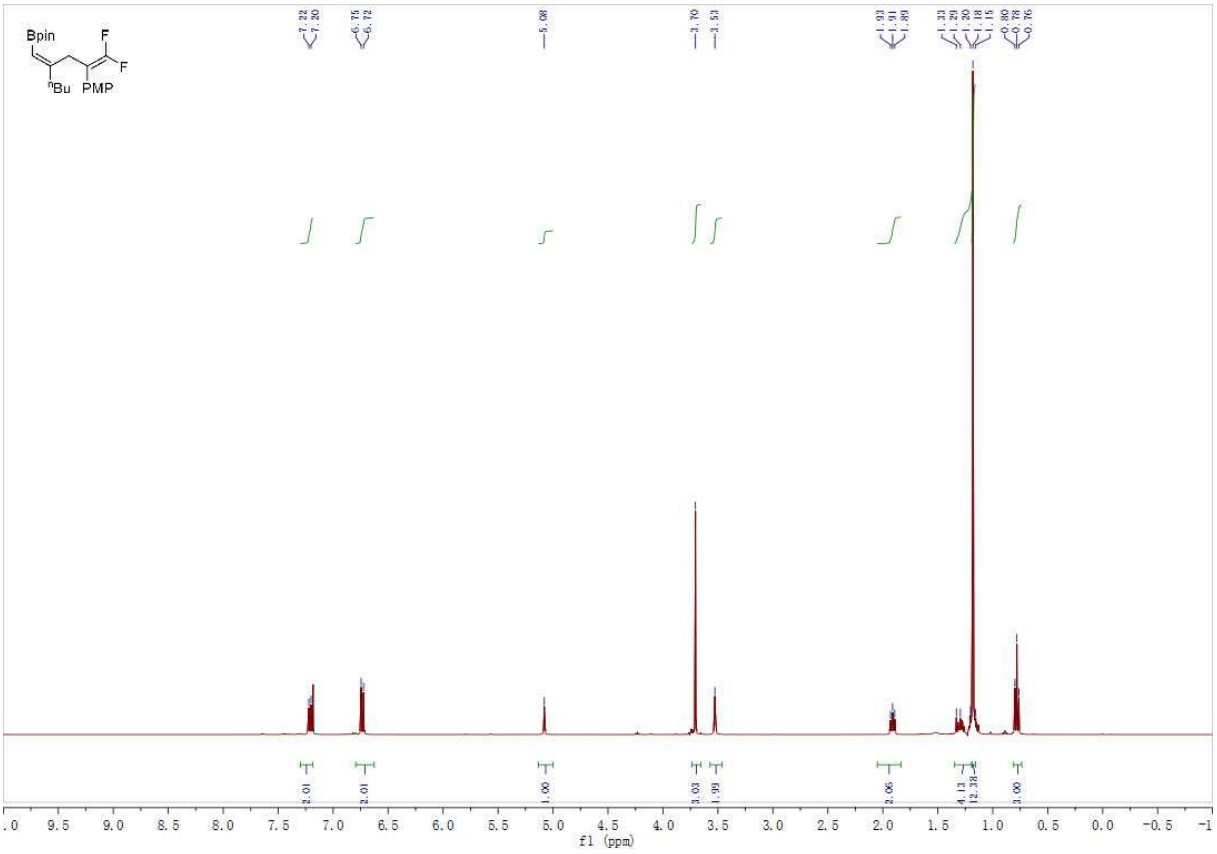


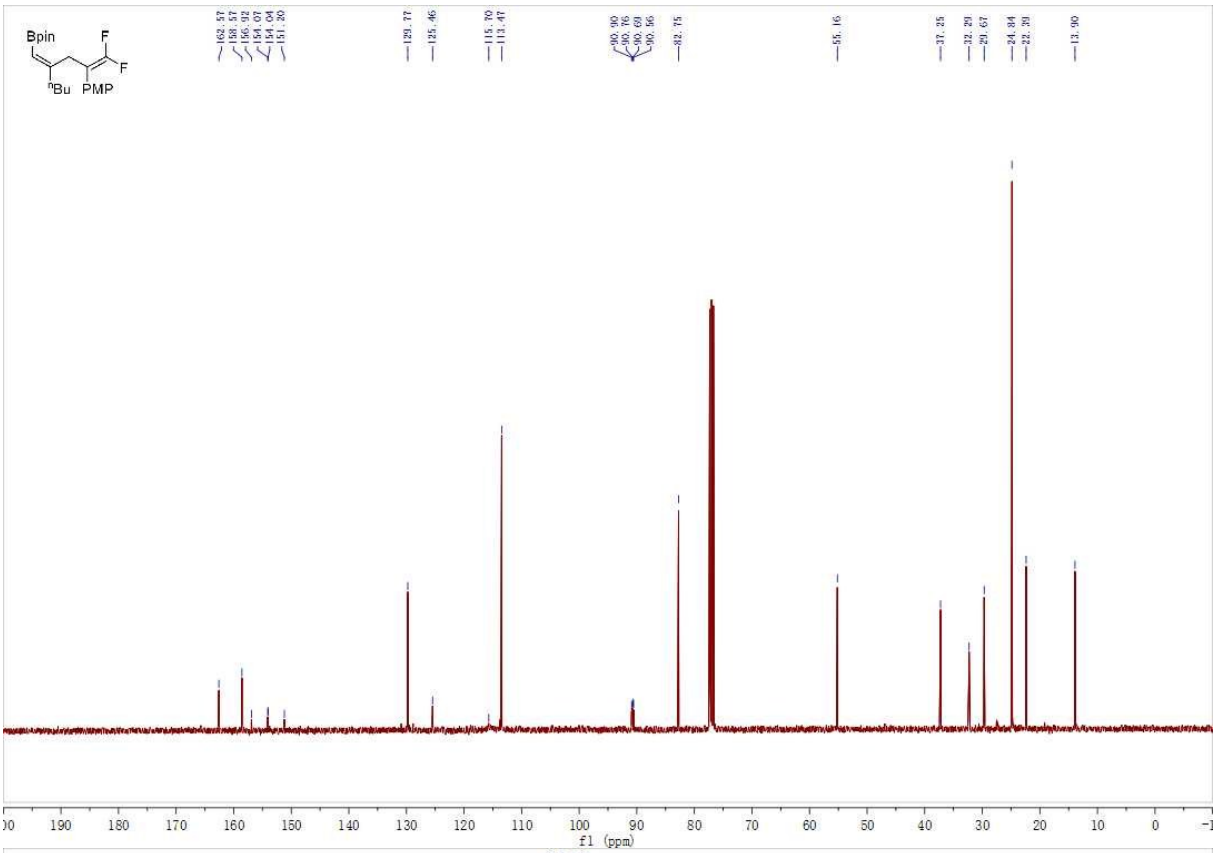
3q

(Z)-2-(2-(3,3-difluoro-2-(4-methoxyphenyl)allyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (50:1) as thick oil (66 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.8 Hz, 2H), 6.73 (d, *J* = 8.9 Hz, 2H), 5.08 (s, 1H), 3.70 (s, 3H), 3.53 (s, 2H), 1.91 (t, *J* = 7.5 Hz, 2H), 1.36 - 1.20 (m, 4H), 1.18 (s, 12H), 0.78 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.57, 158.57, 154.06 (dd, *J* = 289.4, 286.2 Hz), 129.77, 125.46, 115.70, 113.47, 90.73 (dd, *J* = 21.0, 13.6 Hz), 82.75, 55.16, 37.25, 32.29, 29.67, 24.84, 22.39, 13.90. ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.13 (d, *J* = 44.8 Hz), -92.47 (d, *J* = 44.8 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.96. HRMS (ESI^{+}): Calcd for $C_{22}H_{31}BF_2O_3$ [H]$^{+}$: 393.2413, Found: 393.2419.




Bpin
F
F
nBu
PMP
162.57
158.57
156.92
154.07
154.04
151.20
129.77
125.46
115.70
113.47
90.90
90.76
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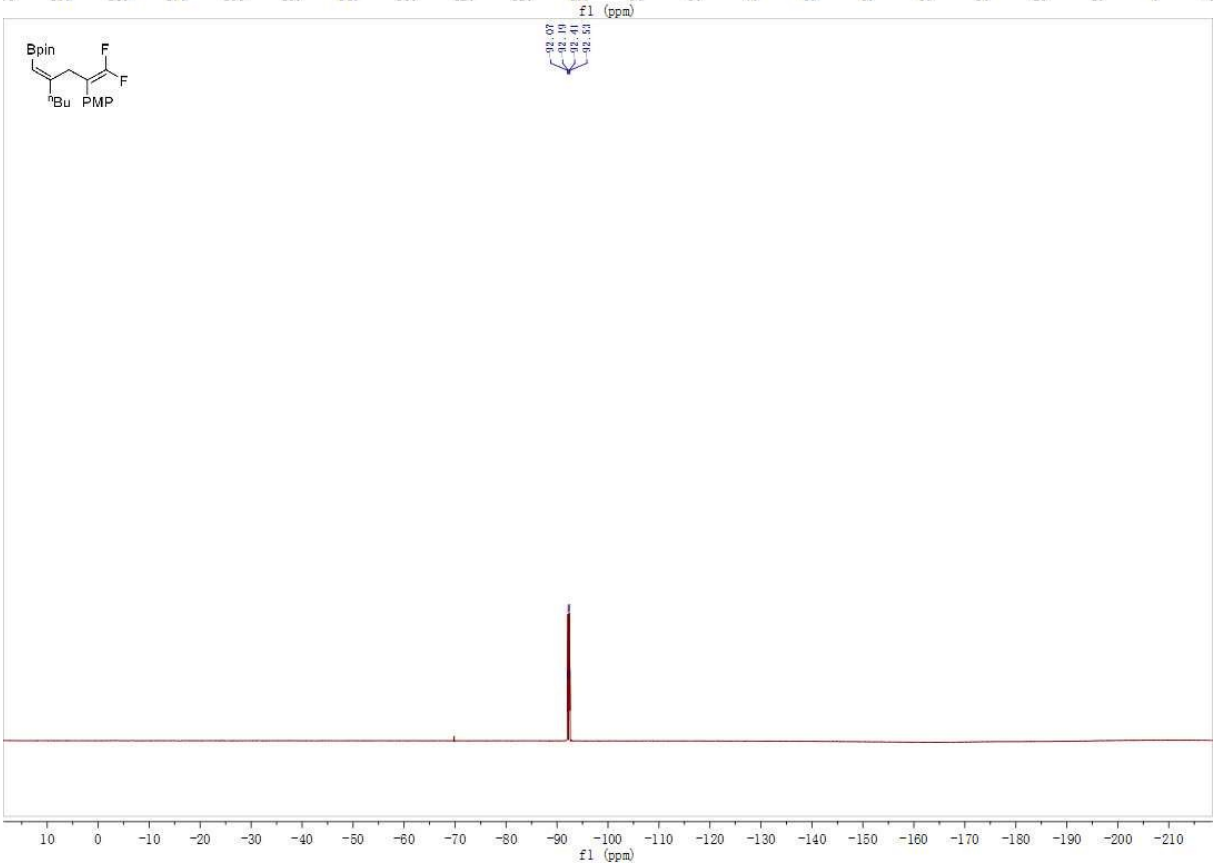
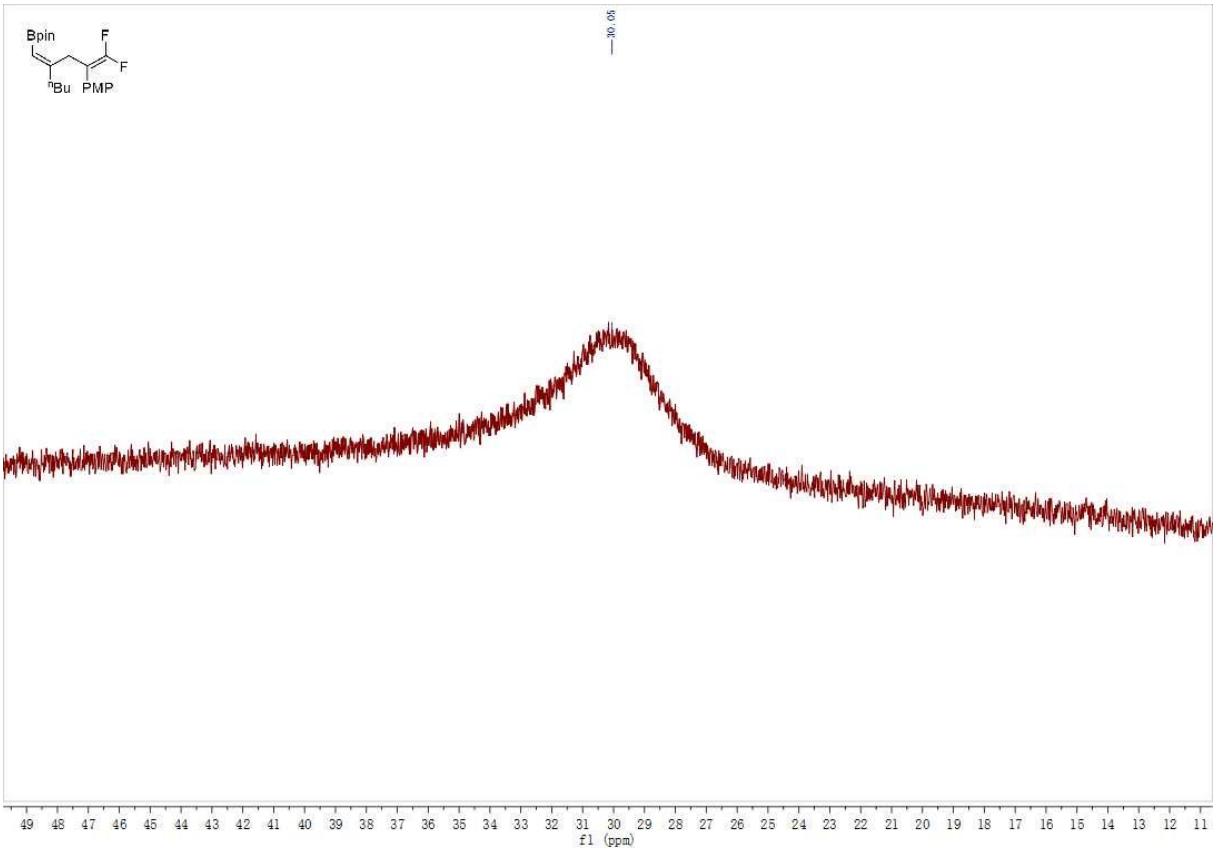
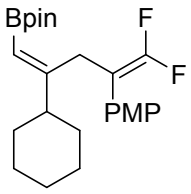
29.67
24.84
22.39
13.90
f1 (ppm)

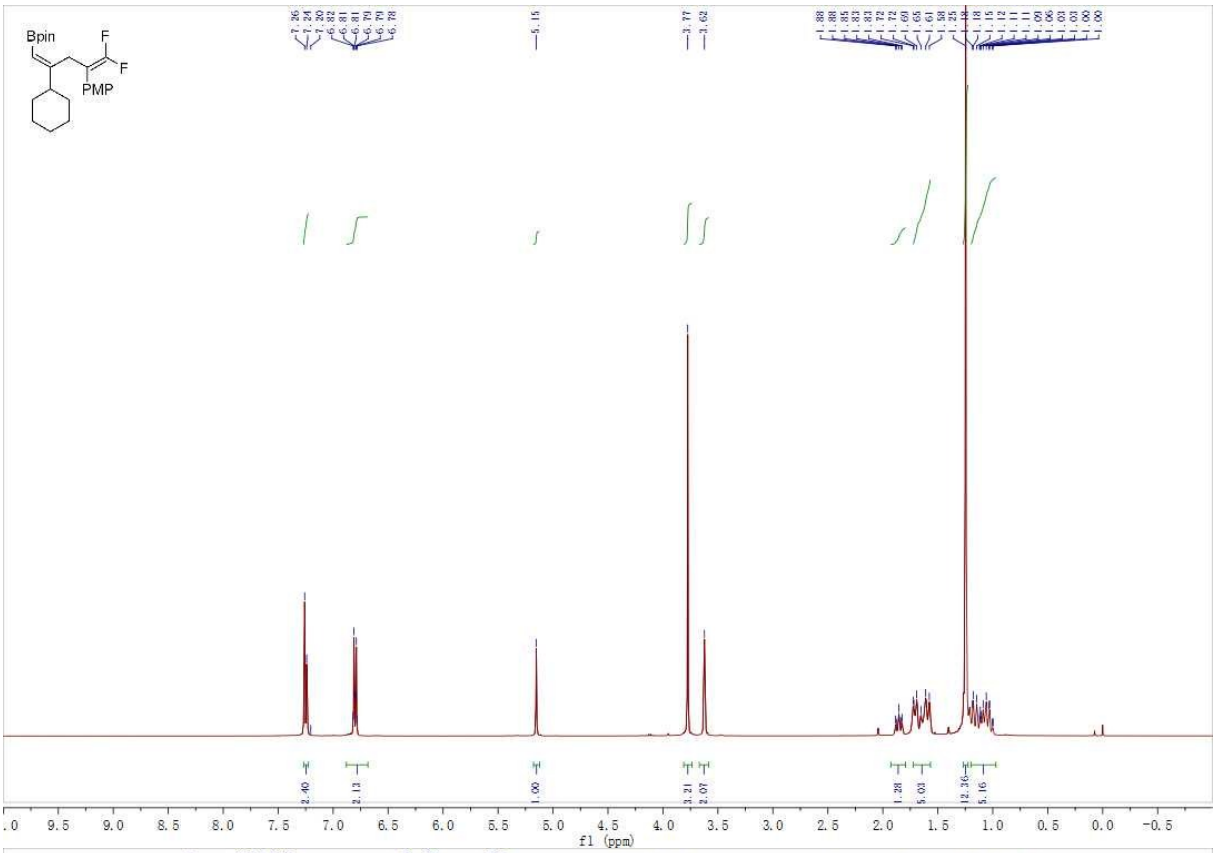

Bpin
F
F
nBu
PMP
-92.07
-92.19
-92.41
-92.53
f1 (ppm)

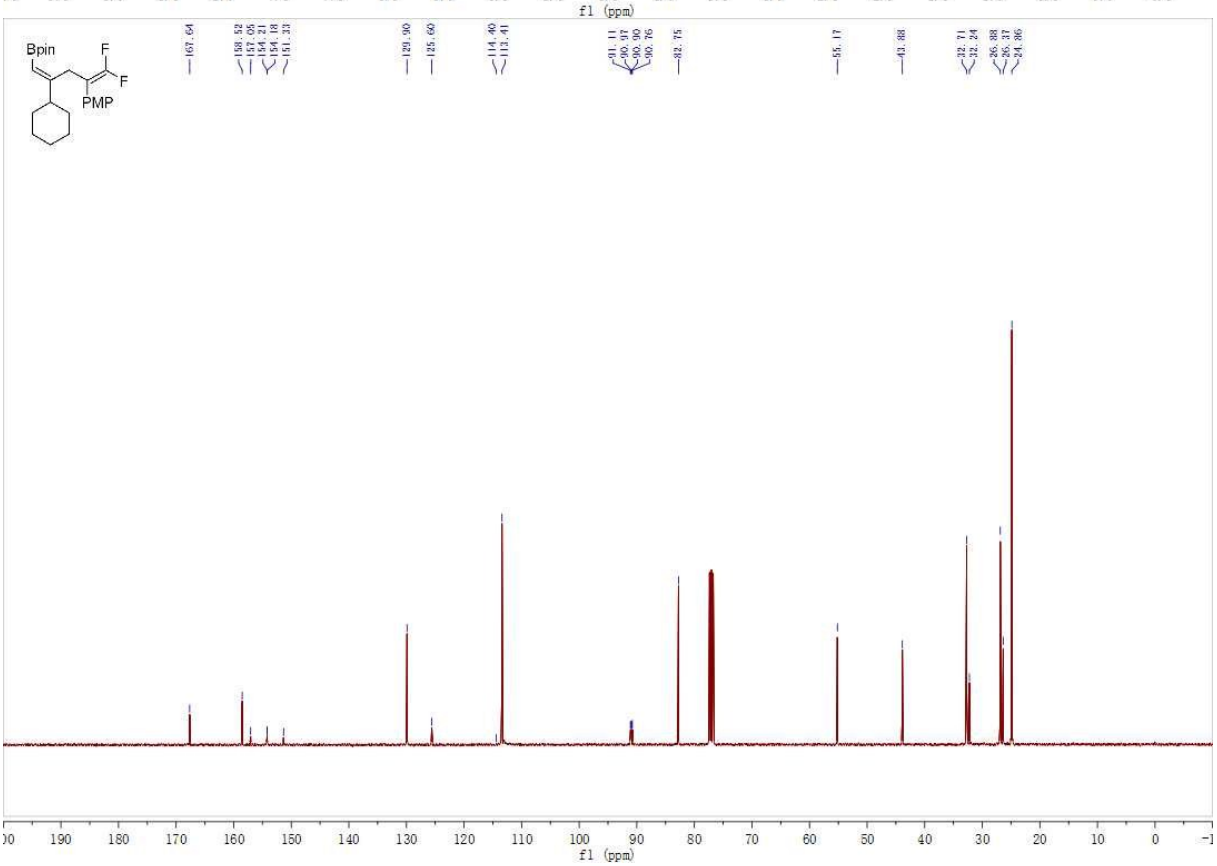


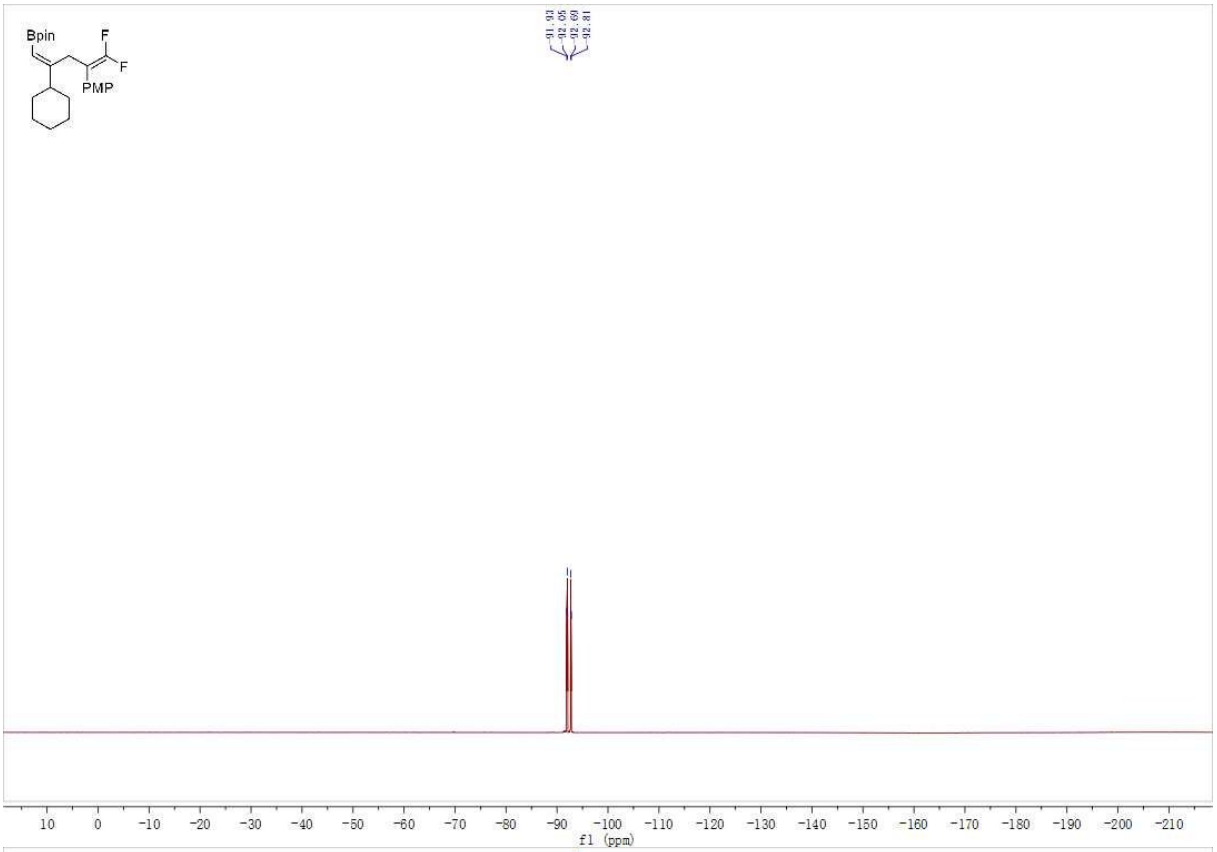
(E)-2-(2-cyclohexyl-5,5-difluoro-4-(4-methoxyphenyl)penta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

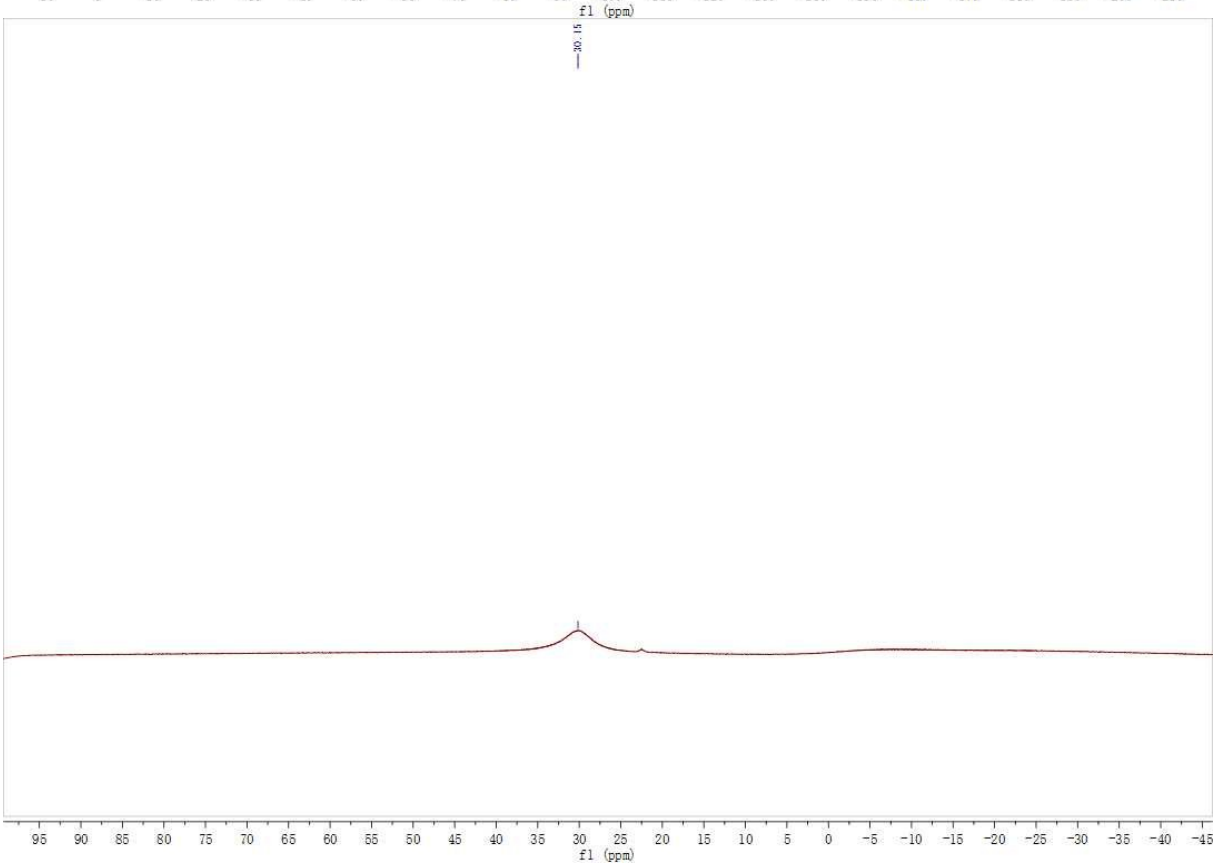


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (66 mg, 79 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.10 (m, 2H), 6.91 - 6.68 (m, 2H), 5.15 (s, 1H), 3.77 (s, 3H), 3.62 (s, 2H), 1.95 - 1.76 (m, 1H), 1.78 - 1.53 (m, 5H), 1.25 (s, 12H), 1.23 - 0.88 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.64, 158.52, 154.19 (dd, J = 289.0, 286.2 Hz), 129.90, 125.60, 114.40, 113.41, 90.93 (dd, J = 21.0, 13.6 Hz), 82.75, 55.17, 43.88, 32.71, 32.24, 26.88, 26.37, 24.86. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.99 (d, J = 44.7 Hz), -92.75 (d, J = 44.7 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.15. HRMS (ESI^+): Calcd for $C_{24}H_{33}BF_2O_3$ $[H]^+$: 419.2569, Found: 419.2571.

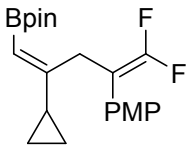

Bpin
F
F
PMP
f1 (ppm)


Bpin
F
F
PMP
f1 (ppm)

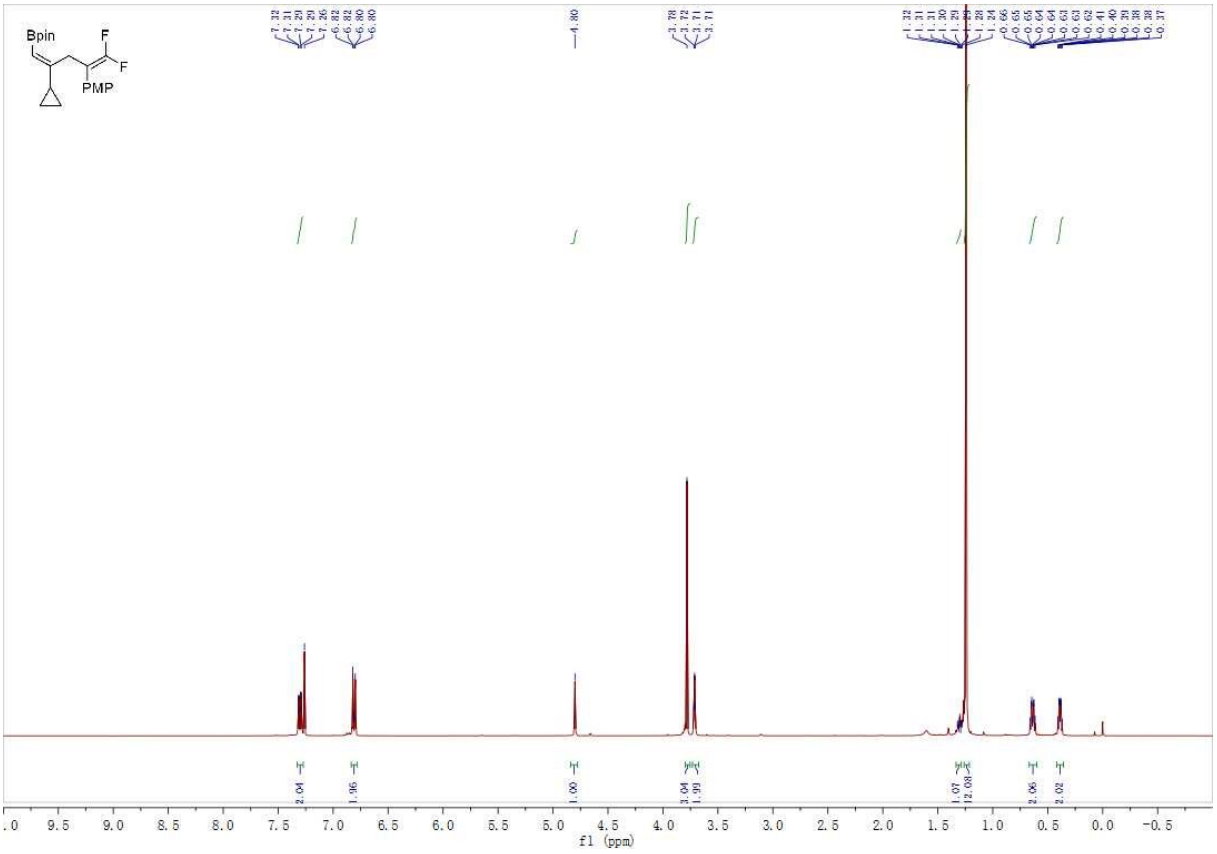

Bpin
F
F
PMP
-91.93
-92.05
-92.69
-92.81
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

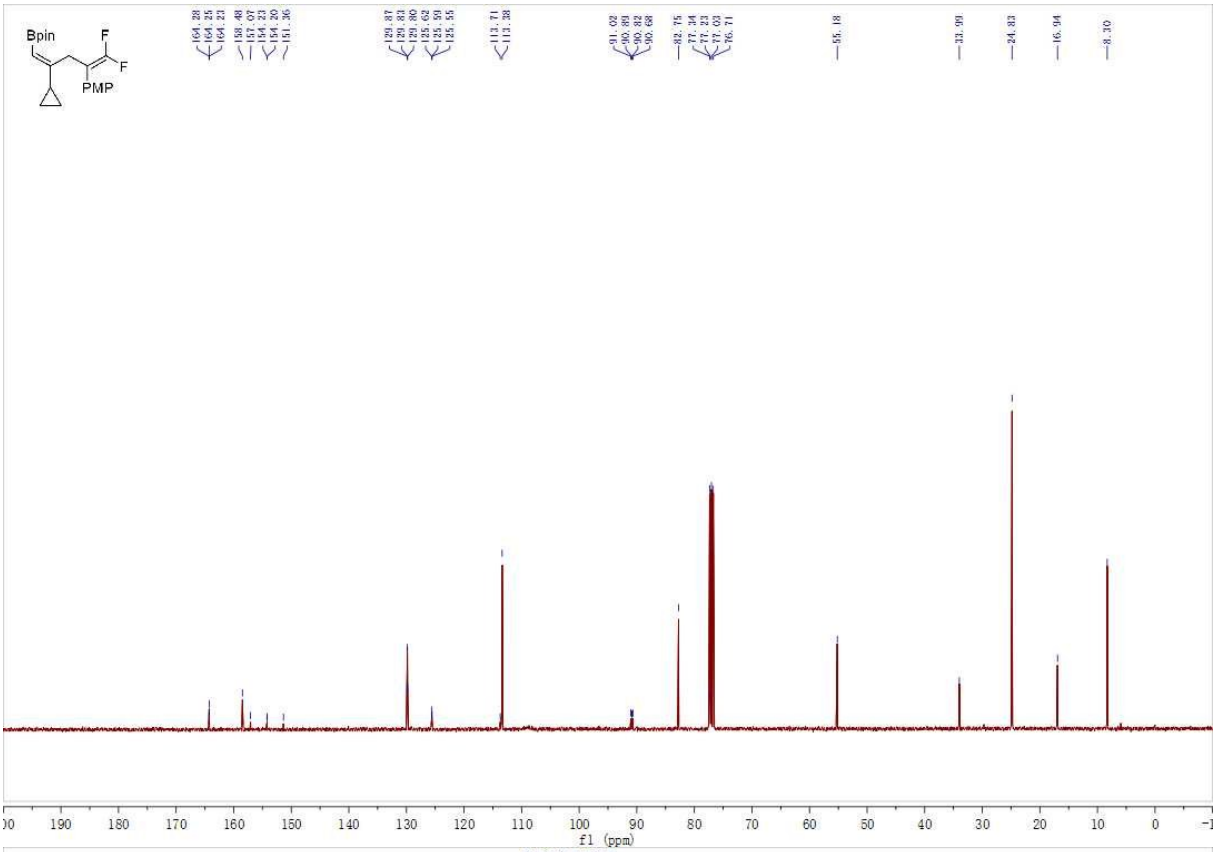

30.15
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

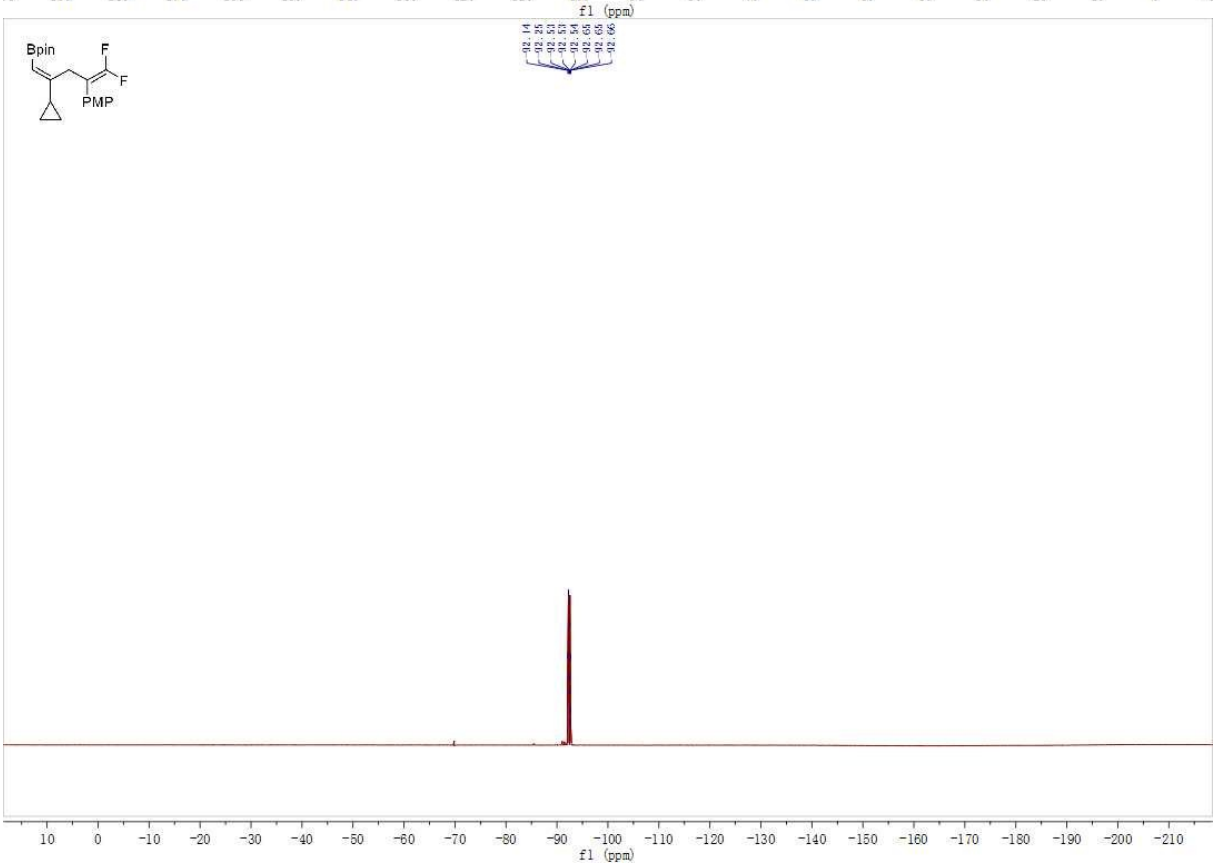
(*E*)-2-(2-cyclopropyl-5,5-difluoro-4-(4-methoxyphenyl)penta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (33.2 mg, 44 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 - 7.27 (m, 2H), 6.84 - 6.77 (m, 2H), 4.80 (s, 1H), 3.78 (s, 3H), 3.71 (t, *J* = 2.3 Hz, 2H), 1.33 - 1.28 (m, 1H), 1.24 (s, 12H), 0.67 - 0.61 (m, 2H), 0.42 - 0.36 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.25 (dd, *J* = 2.4 Hz), 158.48, 154.21 (dd, *J* = 289.0, 286.2 Hz), 129.83 (dd, *J* = 3.2 Hz), 125.59 (dd, *J* = 3.5 Hz), 113.71, 113.38, 90.85 (dd, *J* = 21.0, 13.6 Hz), 82.75, 55.18, 33.99, 24.83, 16.94, 8.30. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -92.19 (d, *J* = 44.4 Hz), -92.59 (d, *J* = 44.4). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.88. HRMS (ESI$^+$): Calcd for $C_{21}H_{27}BF_2O_3$ [H]$^+$: 377.2100, Found: 377.2092.




Bpin
F
F
PMP
164.28
164.25
164.21
158.48
157.07
154.23
154.20
151.36
129.87
129.83
129.80
125.62
125.59
125.55
113.71
113.38
91.02
90.98
90.82
90.68
82.75
77.34
77.23
77.03
76.71
55.18
33.99
24.83
16.94
8.30
f1 (ppm)


Bpin
F
F
PMP
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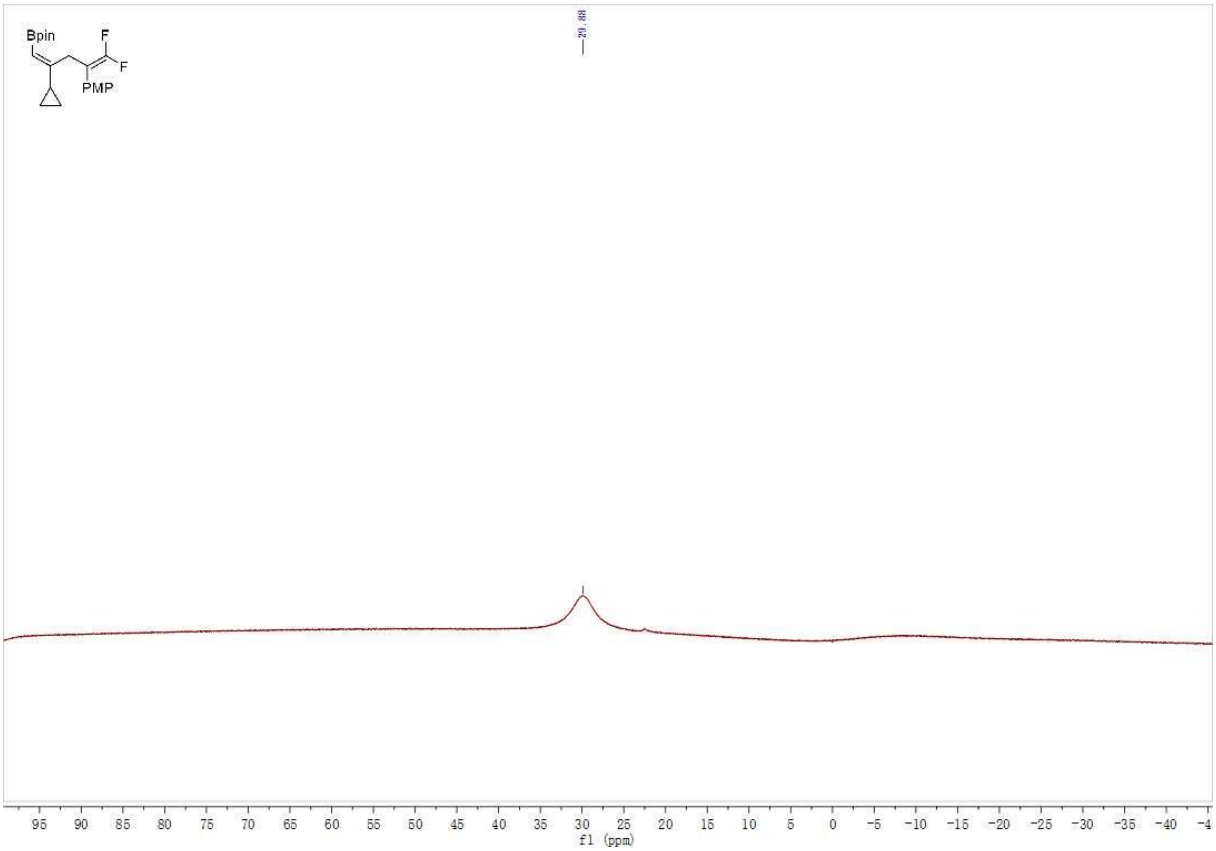
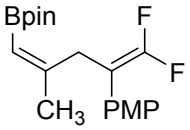
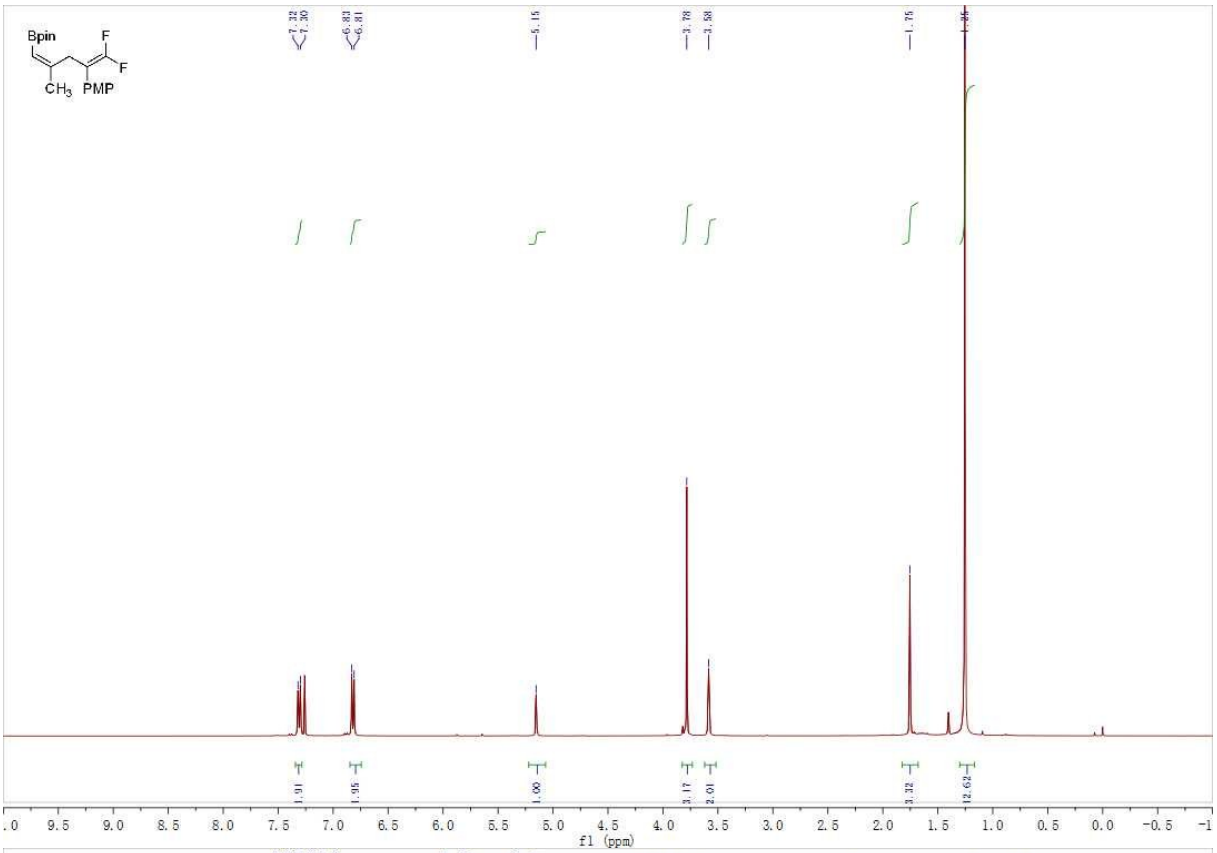
-92.25
-92.51
-92.53
-92.54
-92.65
-92.65
-92.66
f1 (ppm)



(Z)-2-(5,5-difluoro-4-(4-methoxyphenyl)-2-methylpenta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (61 mg, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.15 (s, 1H), 3.78 (s, 3H), 3.58 (s, 2H), 1.75 (s, 3H), 1.25 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.82, 158.56, 154.08 (dd, *J* = 289.4, 286.5 Hz), 129.65, 125.37, 116.87, 113.51, 90.54 (dd, *J* = 20.5, 14.1 Hz), 82.77, 55.19, 33.54, 25.34, 24.84. ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.12 (d, *J* = 44.3 Hz), -92.32 (d, *J* = 44.3 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.58. HRMS (ESI^+): Calcd for $C_{19}H_{25}BF_2O_3$ $[H]^+$: 351.1943, Found: 351.1948.


Bpin
F
F
CH3
PMP
7.32
7.30
6.83
6.81
5.15
3.78
3.58
1.76
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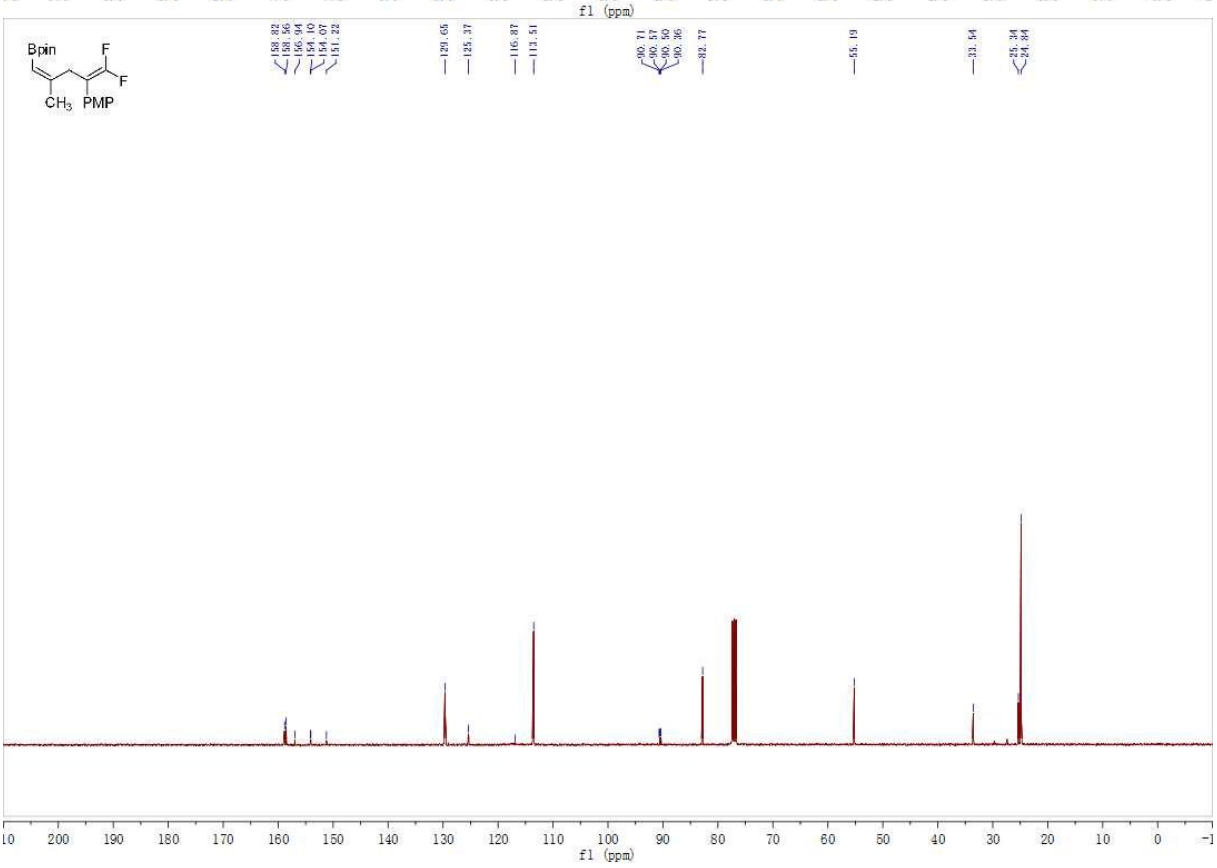
1.91
1.95
1.00
3.17
2.01
3.32
12.62
f1 (ppm)


Bpin
F
F
CH3
PMP
158.82
158.56
156.94
154.10
154.07
151.22
129.65
125.37
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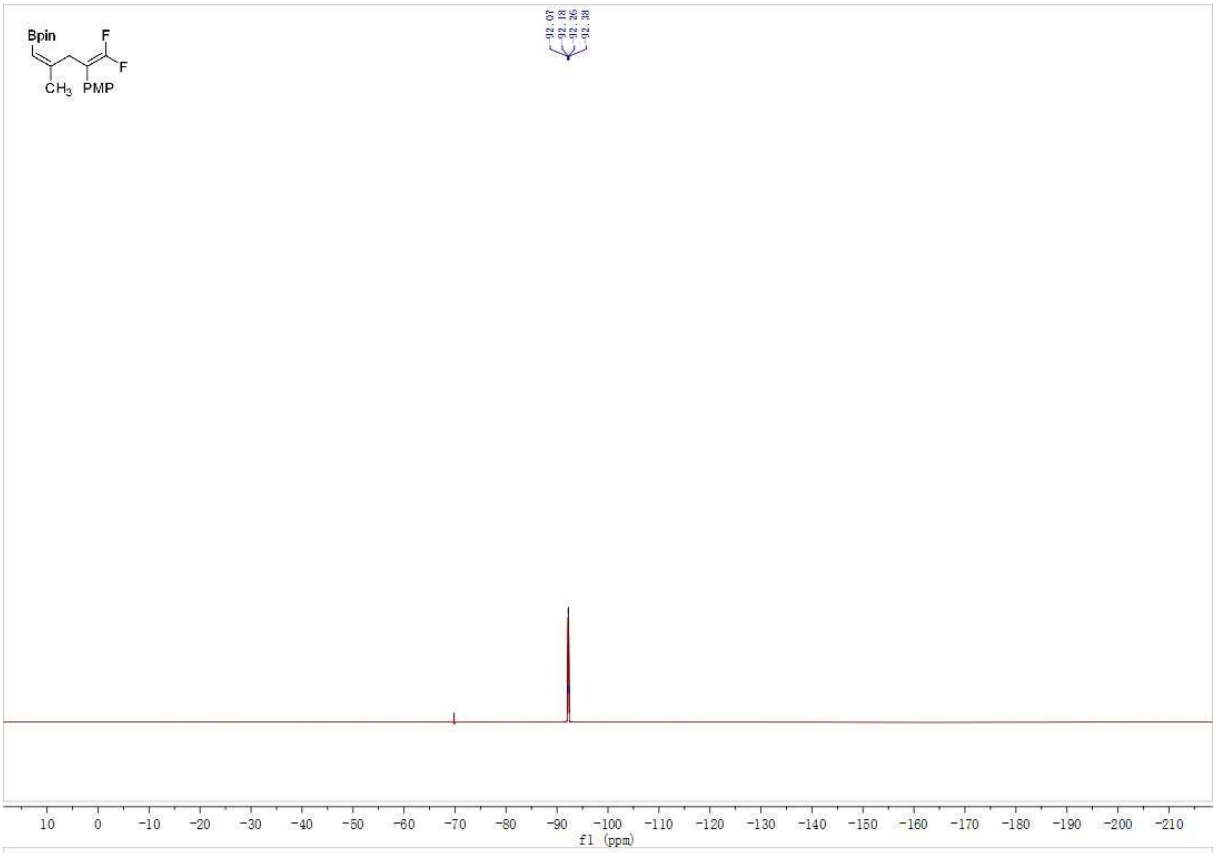
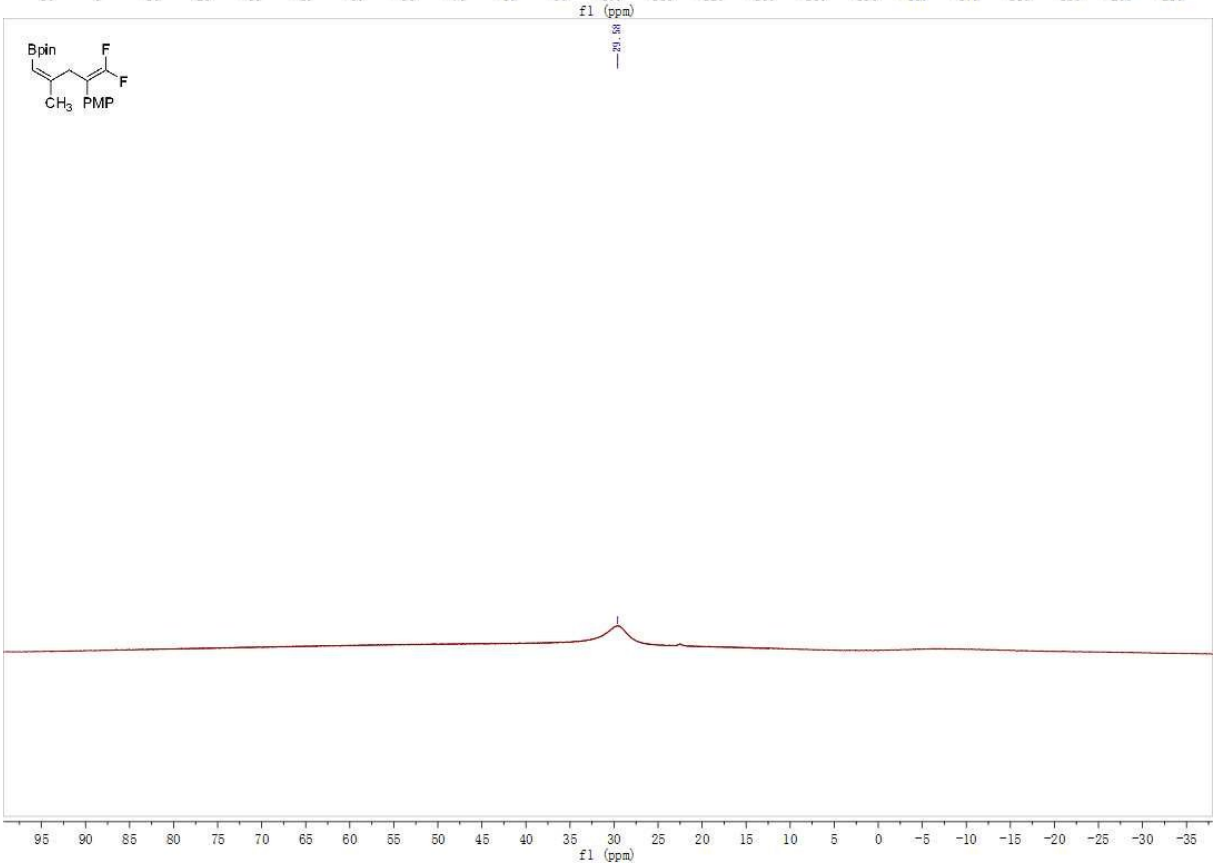
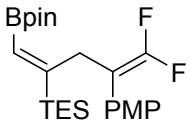
82.77
55.19
33.54
25.34
24.84
f1 (ppm)

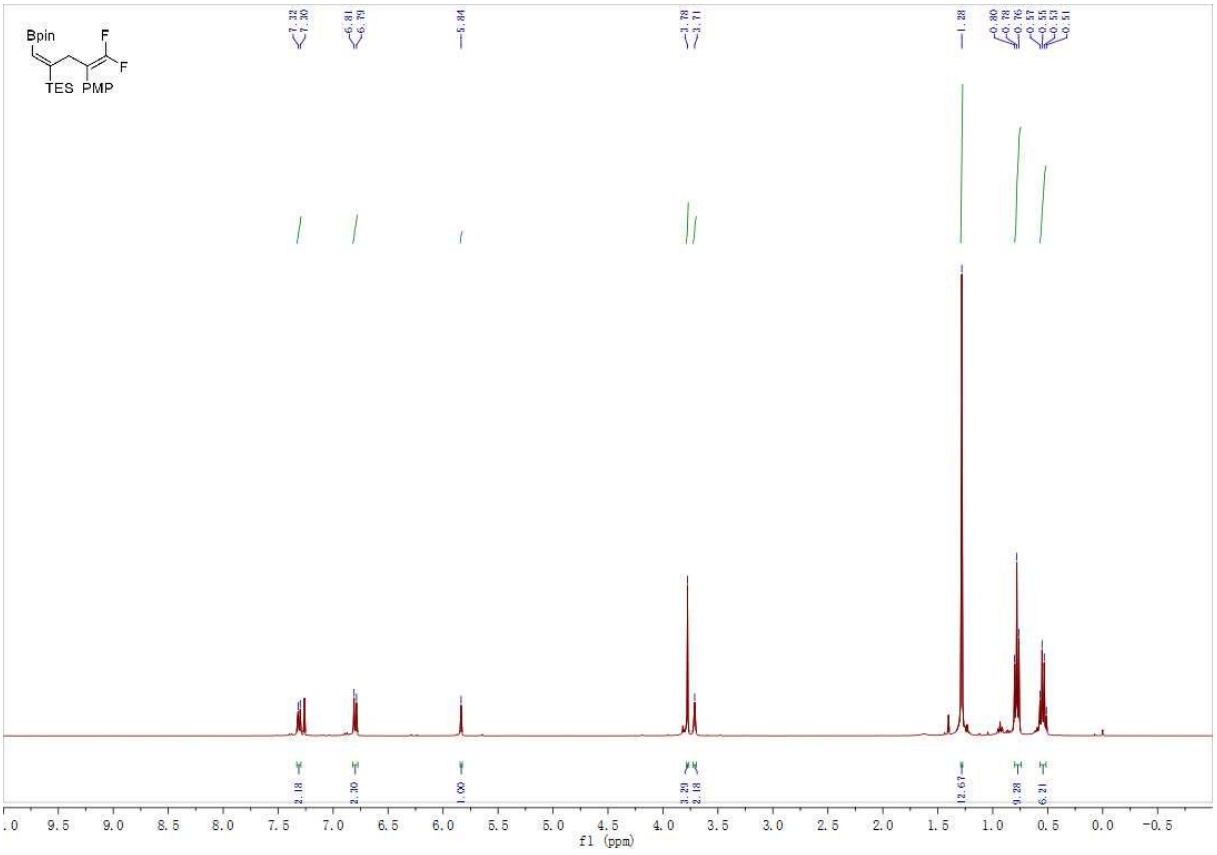

Bpin
F
F
CH3
PMP
-92.07
-92.18
-92.26
-92.38
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

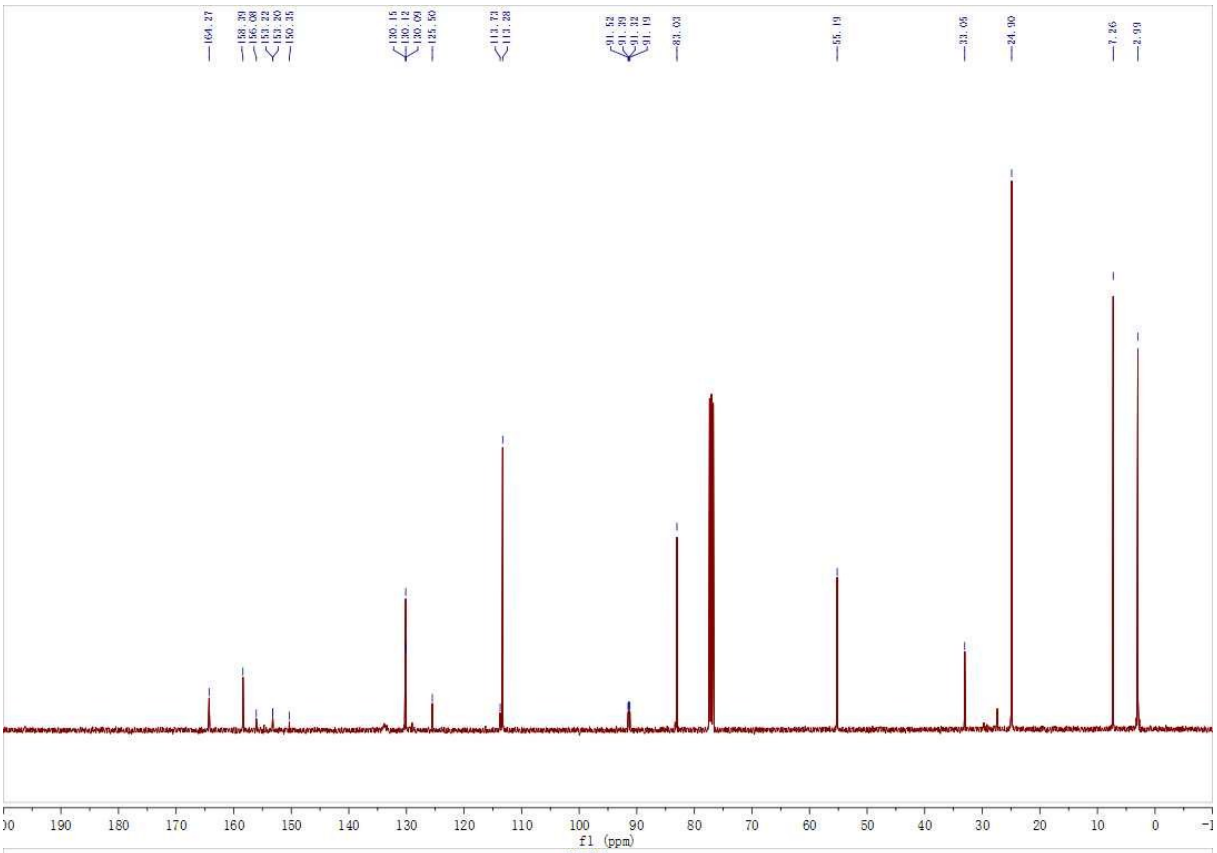

Bpin
F
F
CH3
PMP
29.58
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
f1 (ppm)

(E)-(5,5-difluoro-4-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,4-dien-2-yl)triethylsilane (3e)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (45 mg, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.84 (s, 1H), 3.78 (s, 3H), 3.71 (s, 2H), 1.28 (s, 12H), 0.78 (t, *J* = 7.8 Hz, 9H), 0.54 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.27, 158.39, 153.21 (dd, *J* = 289.6, 286.8 Hz), 130.12, 125.50, 113.73, 113.28, 91.36 (dd, *J* = 20.0, 12.3 Hz), 83.03, 55.19, 33.05, 24.90, 7.26, 2.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.31 (d, *J* = 43.4 Hz), -91.52 (d, *J* = 43.4 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.80. HRMS (ESI^+): Calcd for $C_{24}H_{37}BF_2O_3Si$ $[H]^+$: 451.2651, Found: 451.2647.




164.27
158.39
156.08
153.22
153.00
150.31
130.15
130.12
130.09
125.50
113.73
113.28
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91.32
91.19
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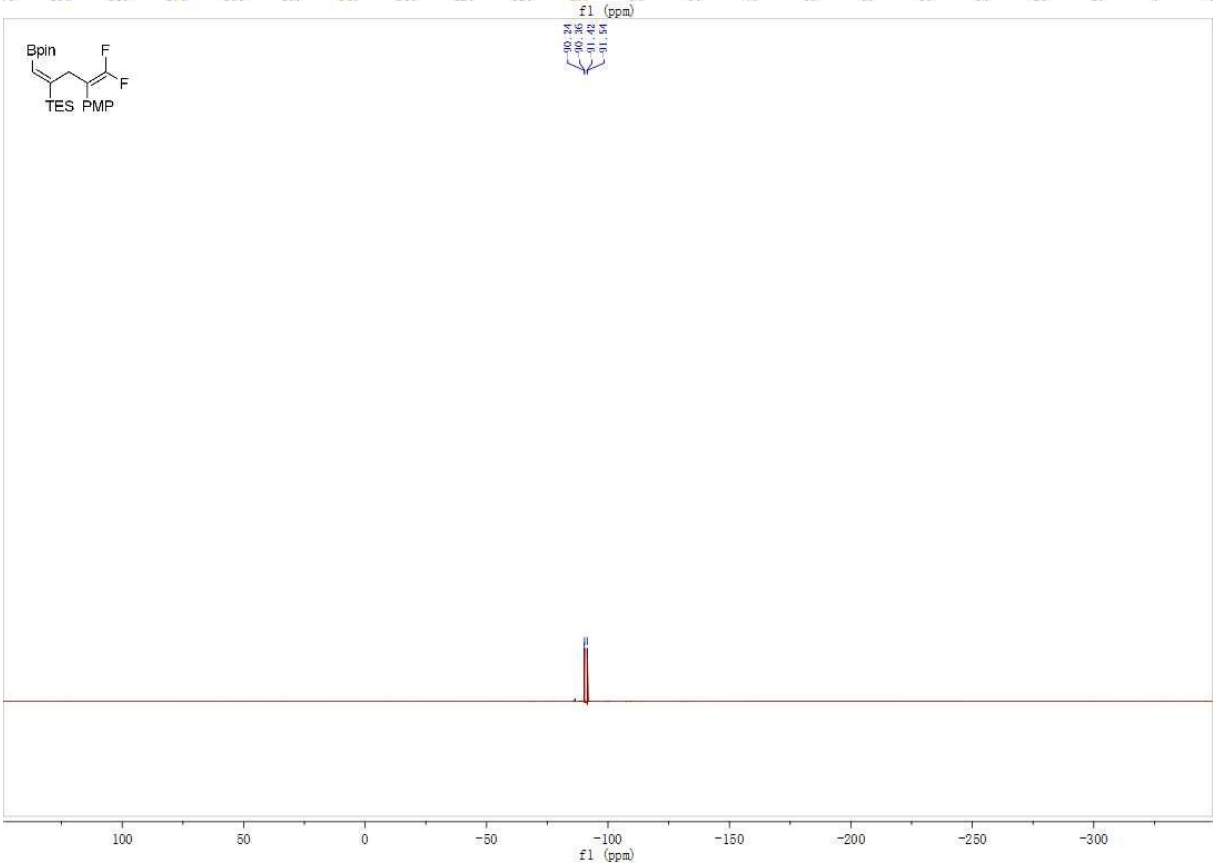
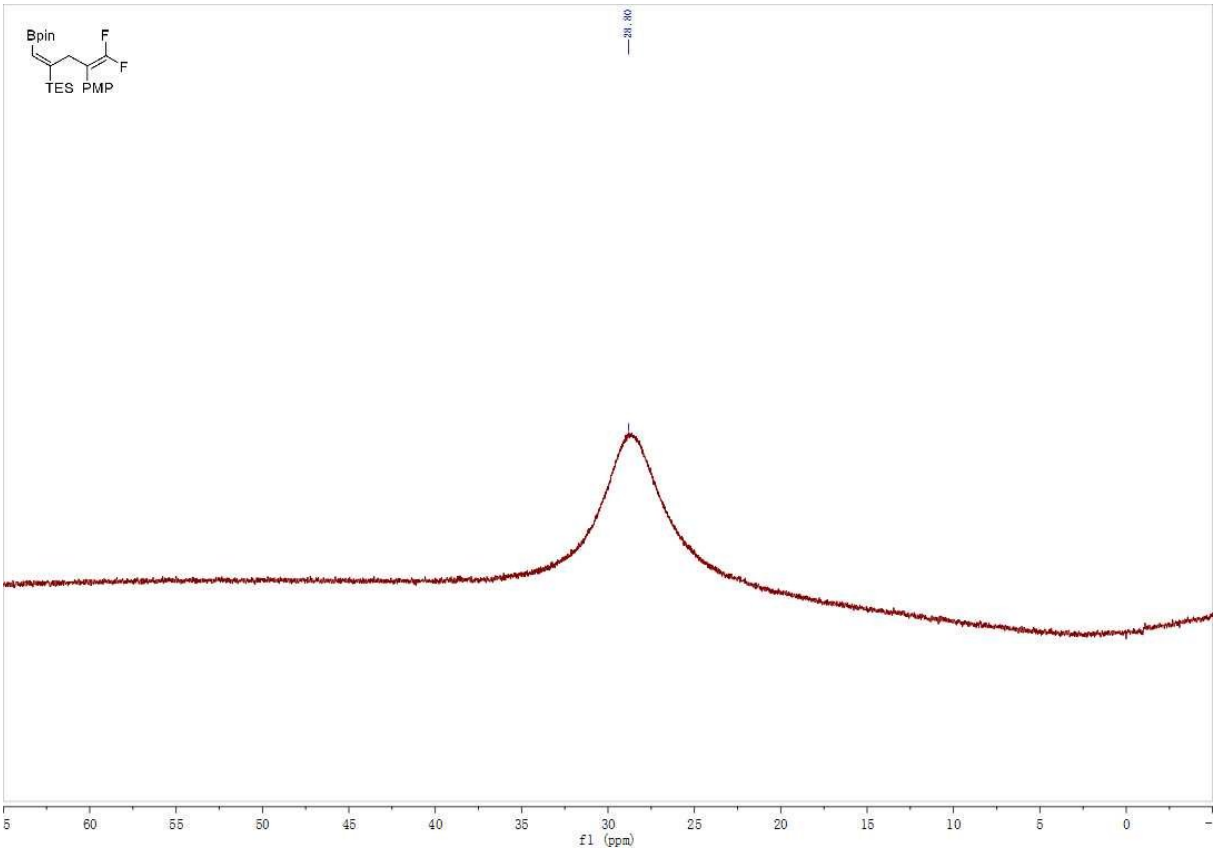
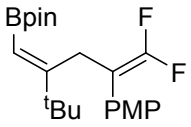
55.19
33.05
24.90
7.26
2.99
f1 (ppm)

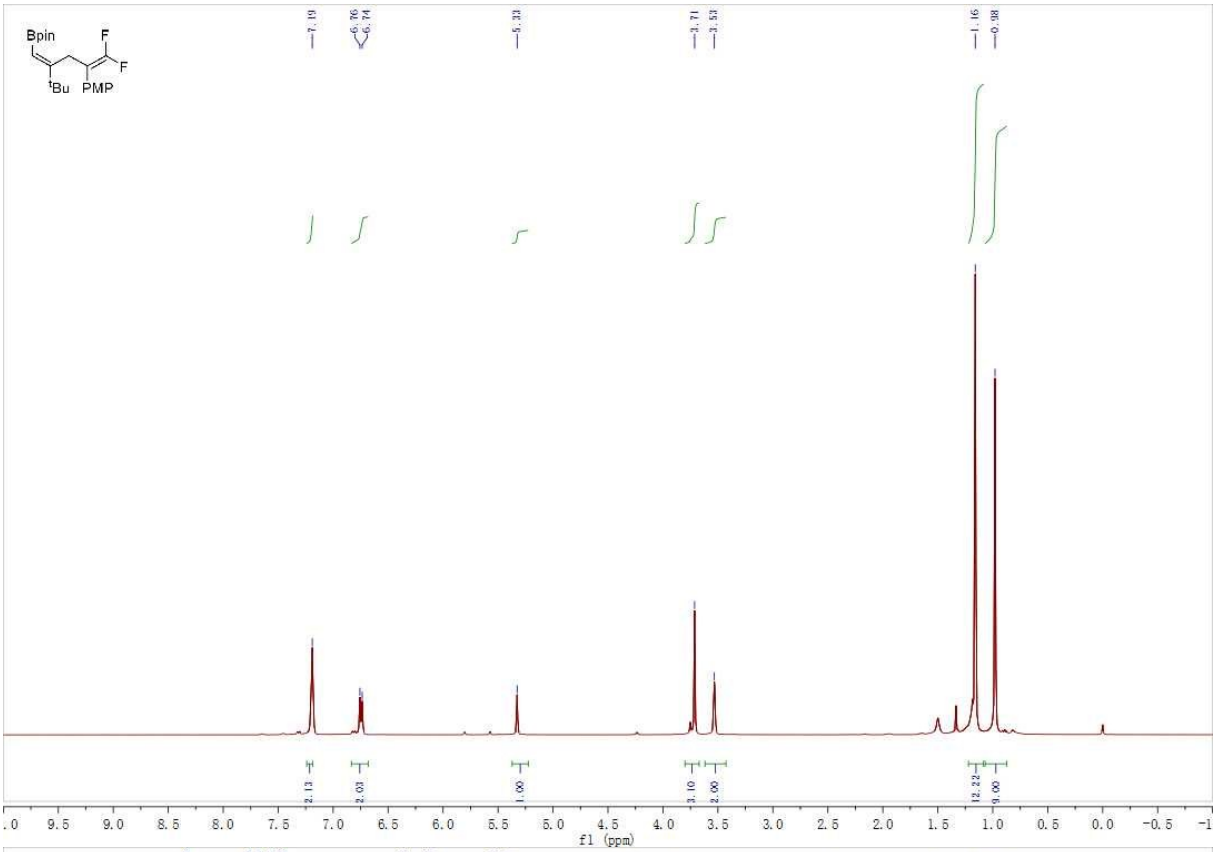

Bpin
F
F
TES
PMP
90.24
90.36
91.42
91.54
f1 (ppm)

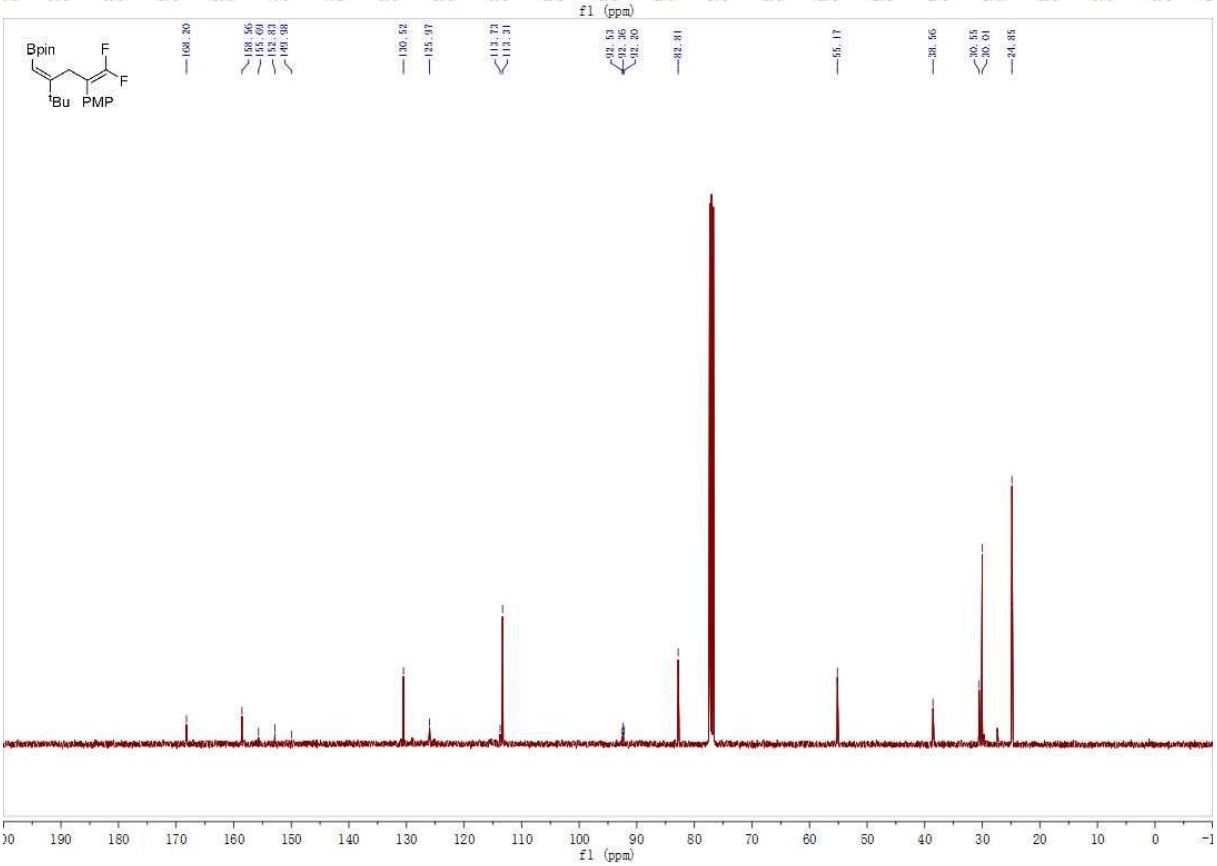


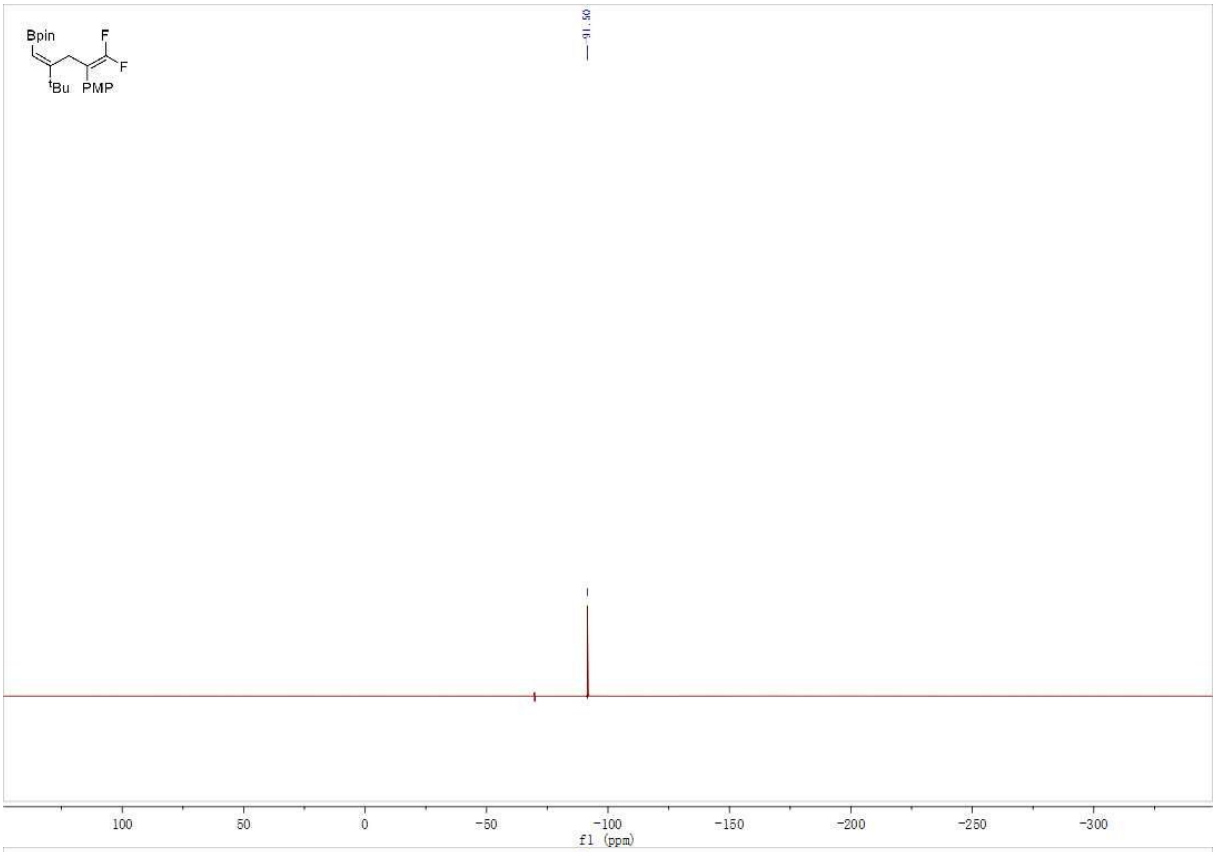
(E)-2-(2-(tert-butyl)-5,5-difluoro-4-(4-methoxyphenyl)penta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

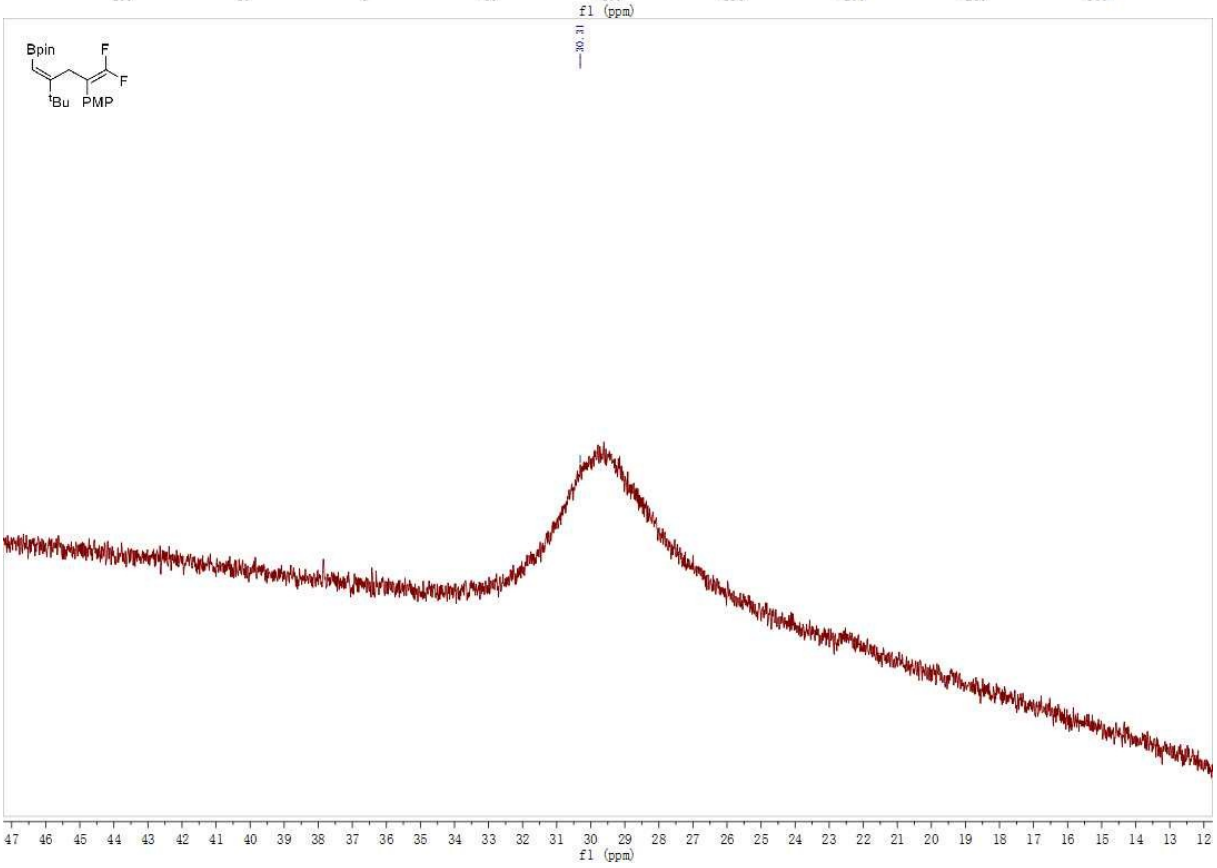


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (36 mg, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.33 (s, 1H), 3.71 (s, 3H), 3.53 (s, 2H), 1.16 (s, 12H), 0.98 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.20, 158.56, 152.83 (dd, *J* = 288.8 Hz), 130.52, 125.97, 113.73, 113.31, 92.36 (dd, *J* = 19.8, 16.1 Hz), 82.81, 55.17, 38.56, 30.55, 30.01, 24.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.51. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.31. HRMS (ESI^+): Calcd for $C_{22}H_{31}BF_2O_3$ $[H]^+$: 393.2413, Found: 393.2409.

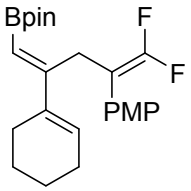

Bpin
F
F
tBu
PMP
7.19
6.76
6.74
5.33
3.71
3.53
1.16
0.98
2.13
2.03
1.00
3.10
2.00
12.22
9.00
f1 (ppm)


Bpin
F
F
tBu
PMP
168.20
158.56
155.69
152.83
149.98
130.52
125.97
113.73
113.31
92.53
92.36
92.20
82.81
55.17
28.56
20.55
20.01
24.85
f1 (ppm)

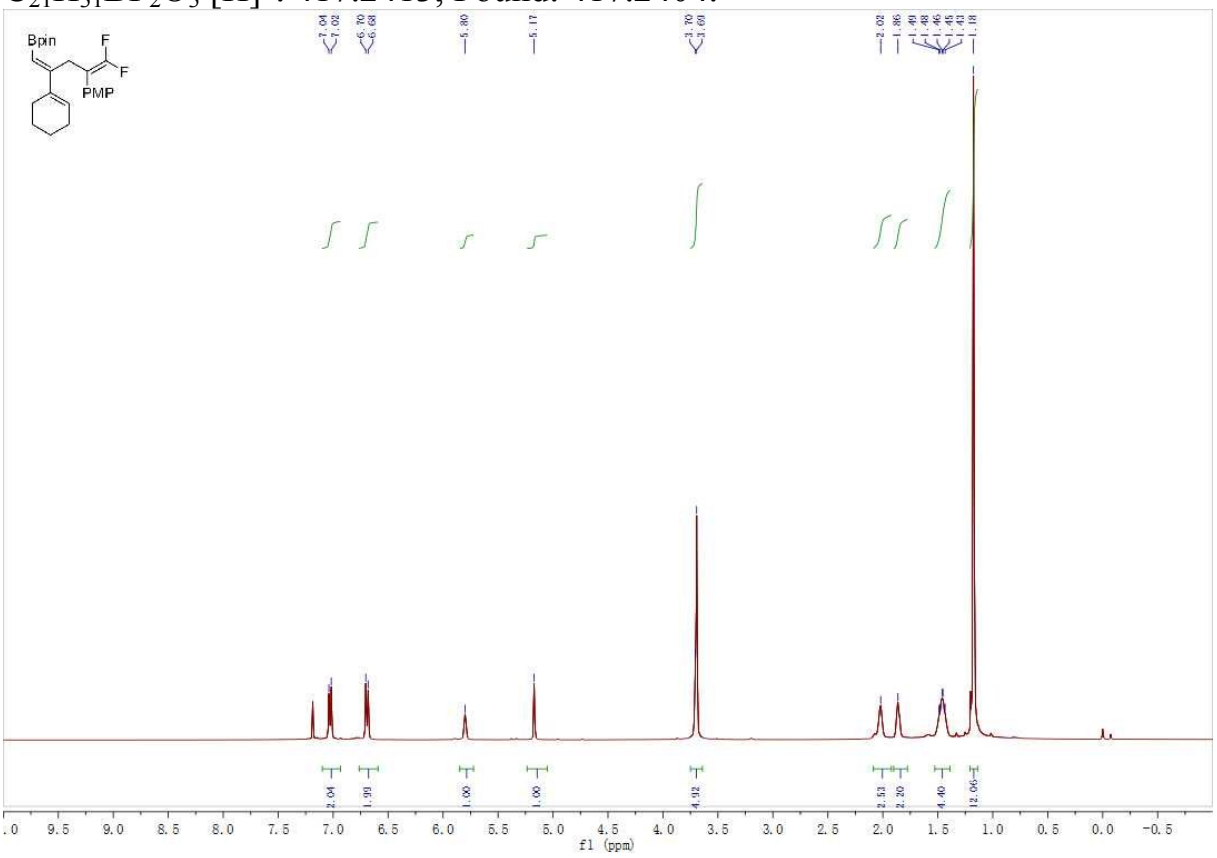

Bpin
F
F
tBu
PMP
-91.50
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

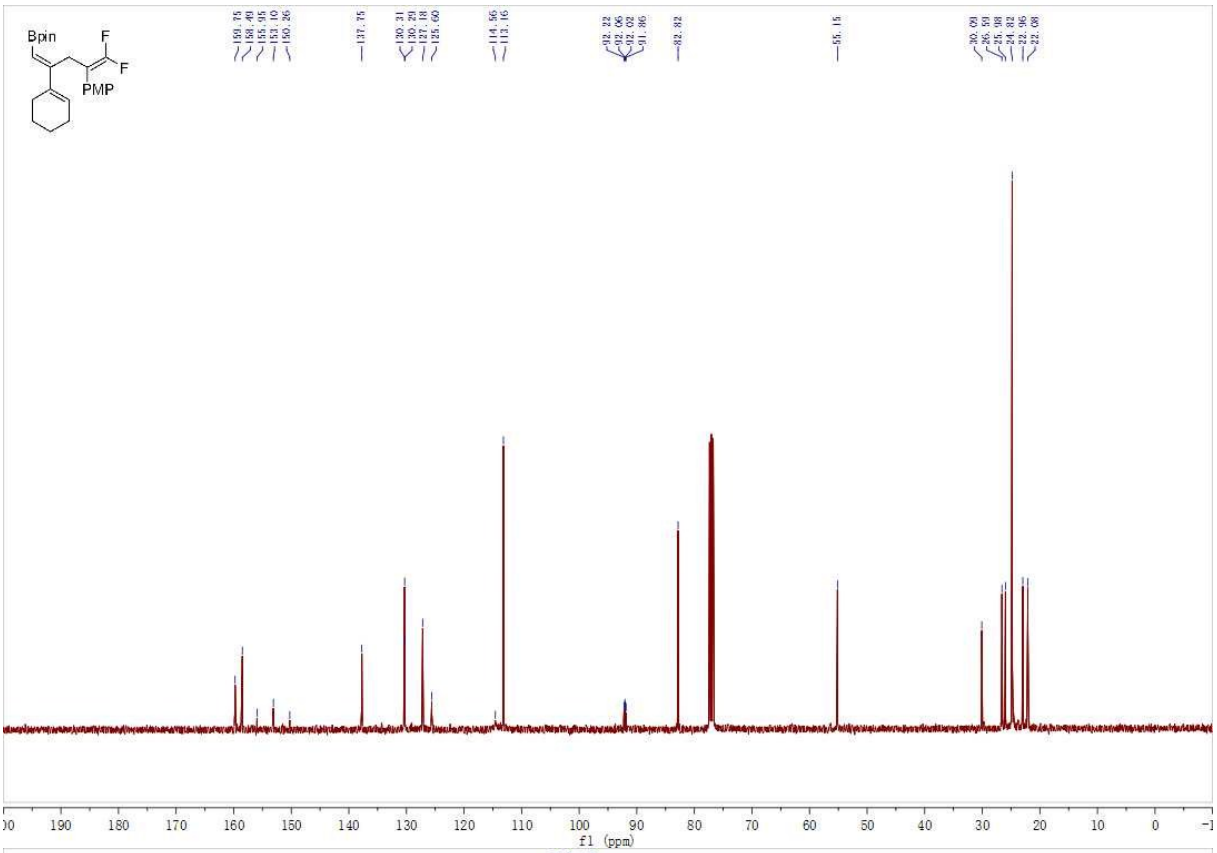

Bpin
F
F
tBu
PMP
30.31
47
46
45
44
43
42
41
40
39
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18
17
16
15
14
13
12
f1 (ppm)

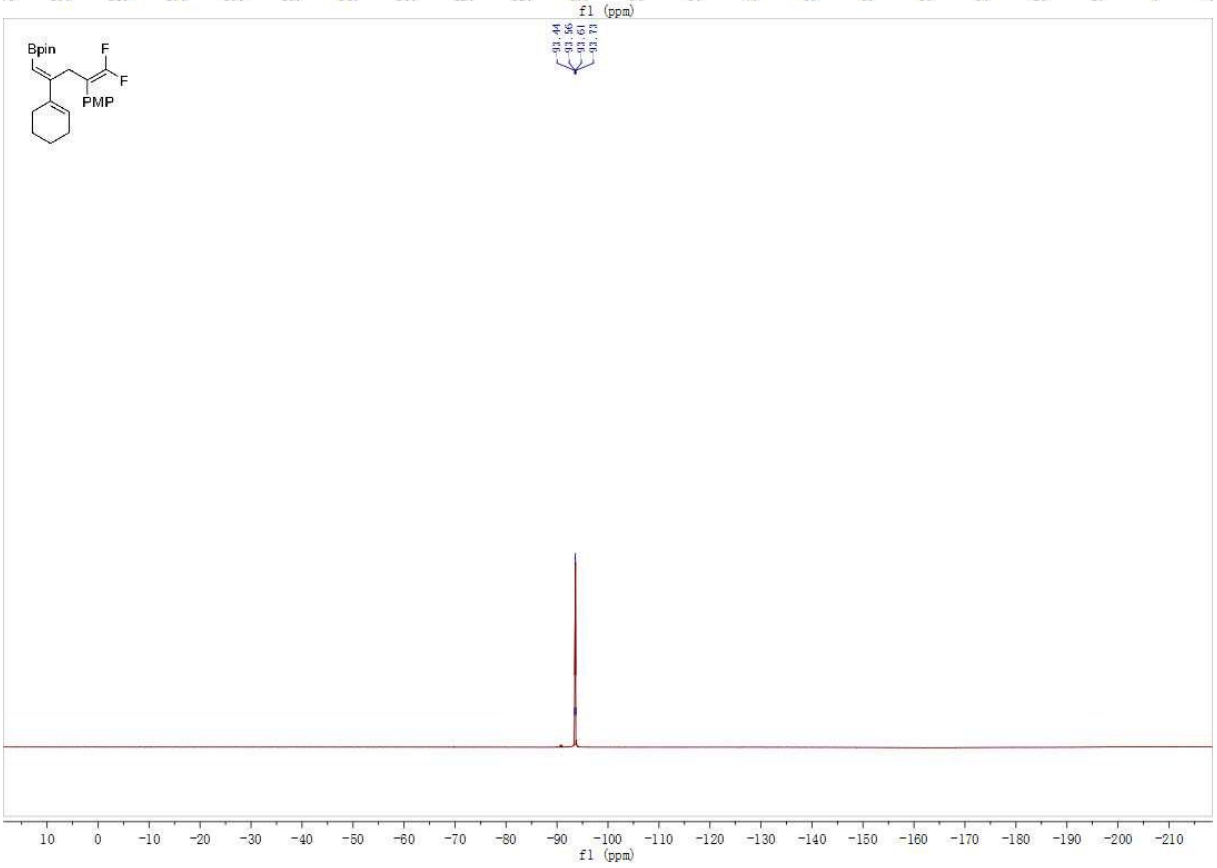
(E)-2-(2-(cyclohex-1-en-1-yl)-5,5-difluoro-4-(4-methoxyphenyl)penta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

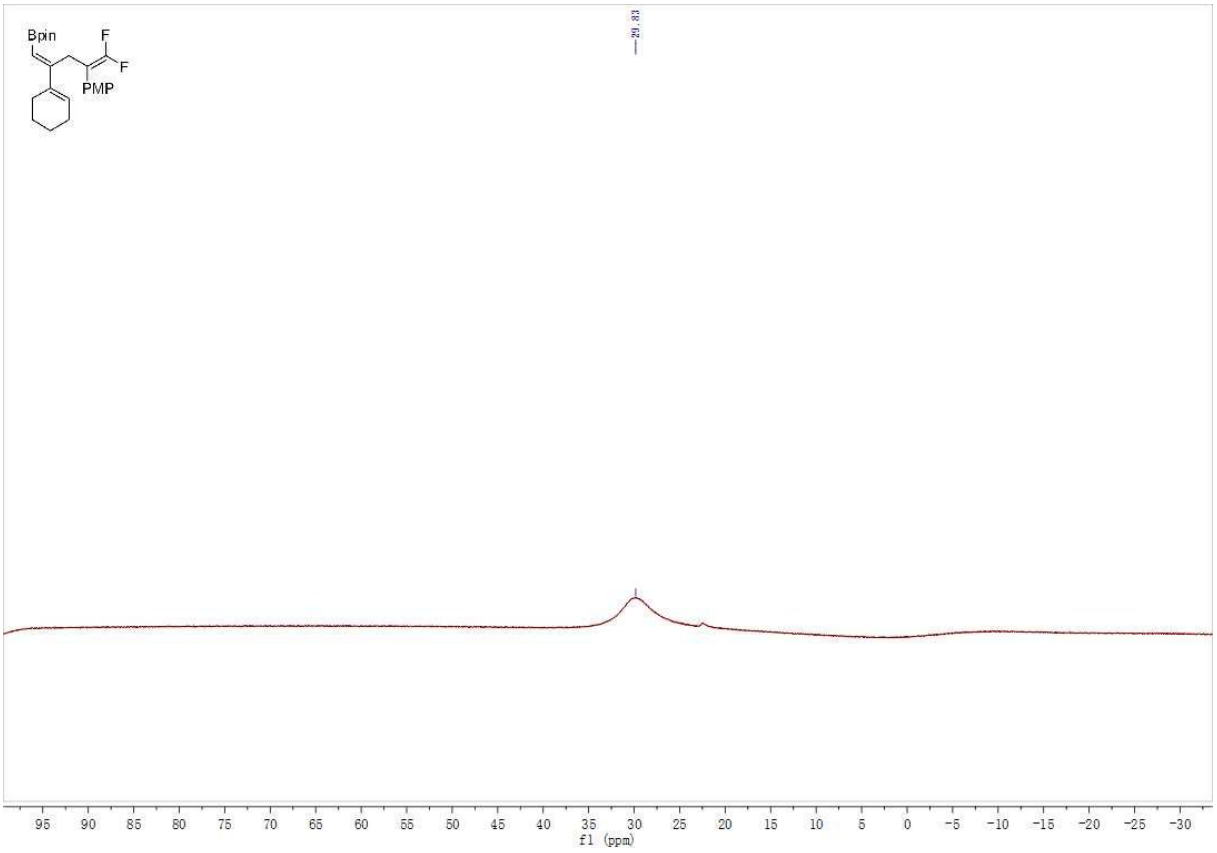


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (50:1) as thick oil (45 mg, 54 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 5.80 (s, 1H), 5.17 (s, 1H), 3.70 (s, 2H), 3.69 (s, 3H), 2.02 (s,2H), 1.86 (s, 2H), 1.54 - 1.41 (m, 4H), 1.18 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.75 , 158.49, 153.10 (dd, *J* = 287.8,286.8 Hz), 137.75, 130.30, 127.18, 125.60, 114.56, 113.16, 92.04 (dd, *J* = 19.8, 16.1 Hz), 82.82, 55.15, 30.09, 26.59, 25.98, 24.82, 22.96, 22.08. ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.50 (d, *J* = 47.1 Hz), -93.67 (d, *J* = 47.1 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.83. HRMS (ESI^{+}): Calcd for $C_{21}H_{31}BF_2O_3$ [H]$^{+}$: 417.2413, Found: 417.2404.

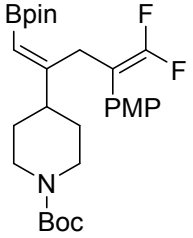



Bpin
F
F
PMP
159.75
158.49
155.15
153.10
150.26
137.75
130.31
130.29
127.18
125.60
114.56
113.16
92.22
92.06
92.02
91.86
82.82
55.15
30.09
26.59
25.98
24.82
22.96
22.08
f1 (ppm)

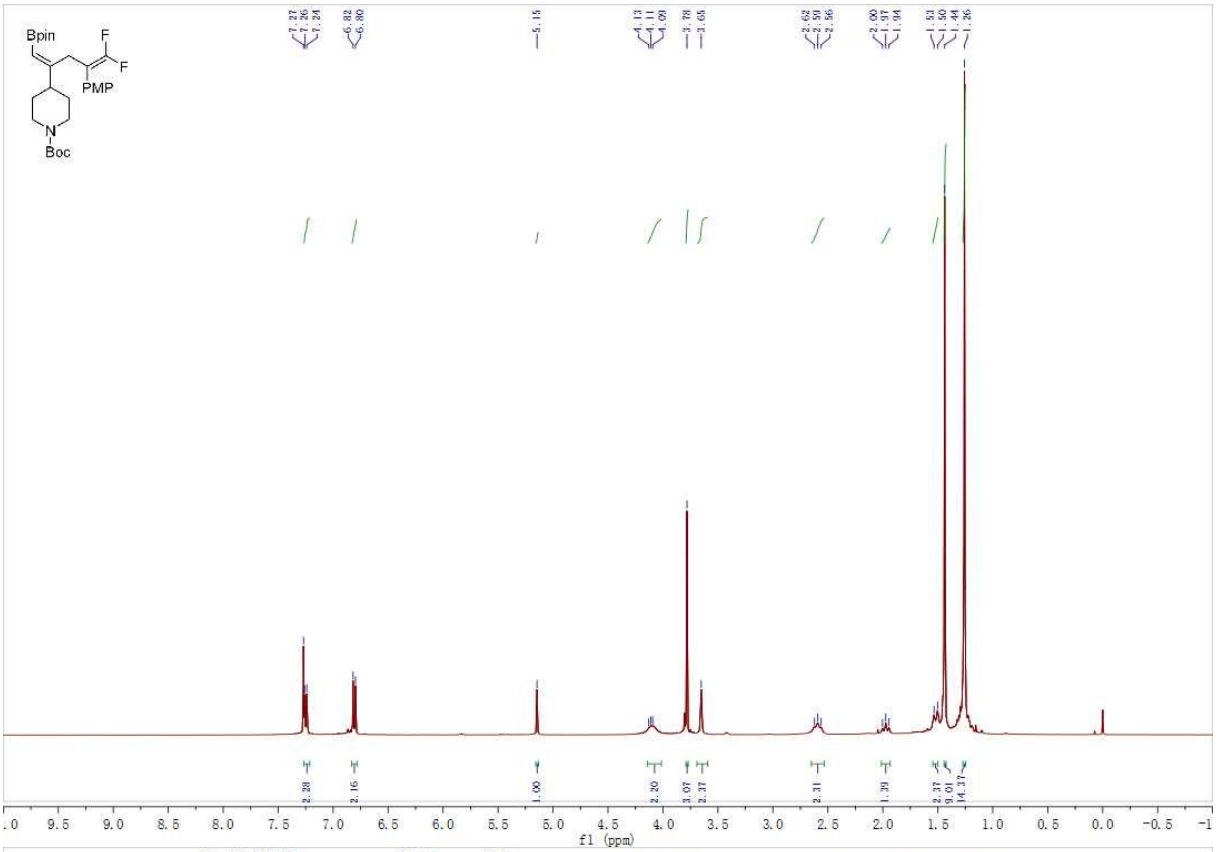

Bpin
F
F
PMP
93.44
93.56
93.61
93.73
f1 (ppm)

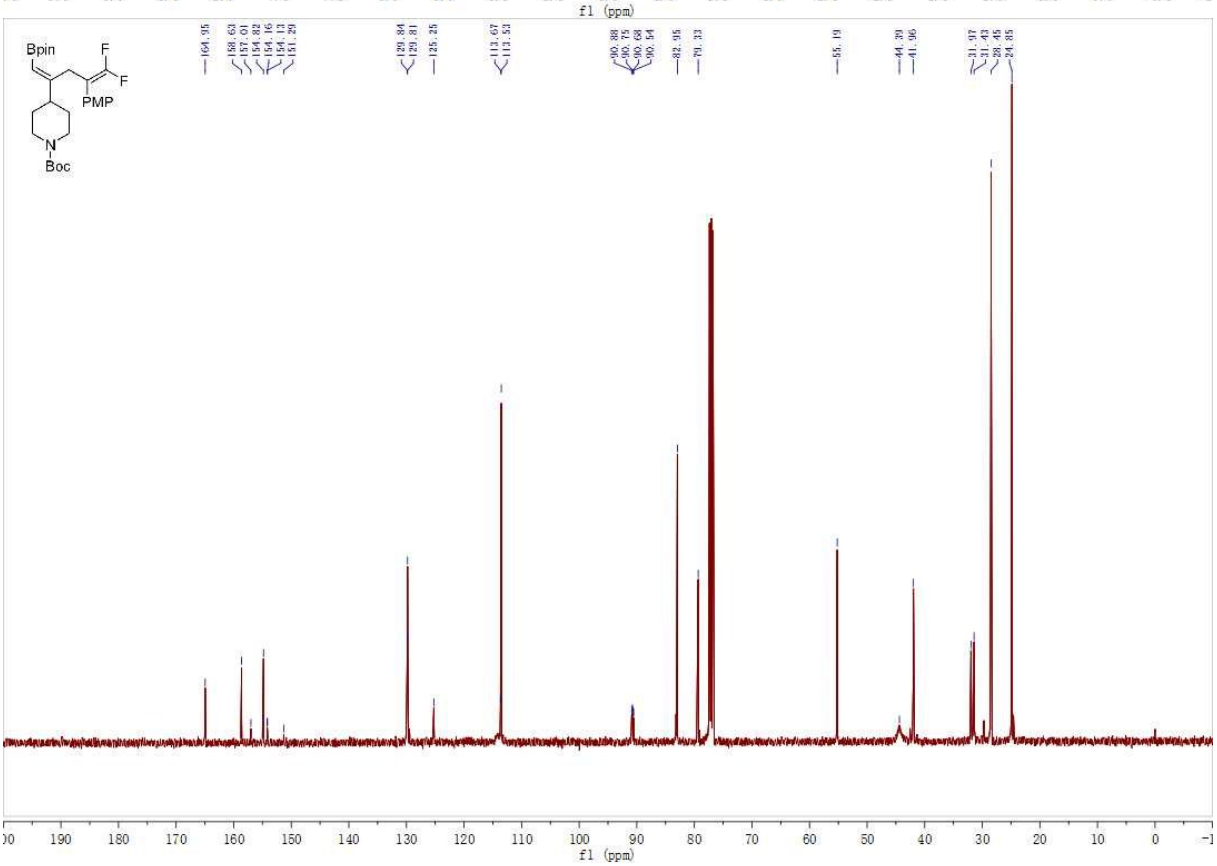


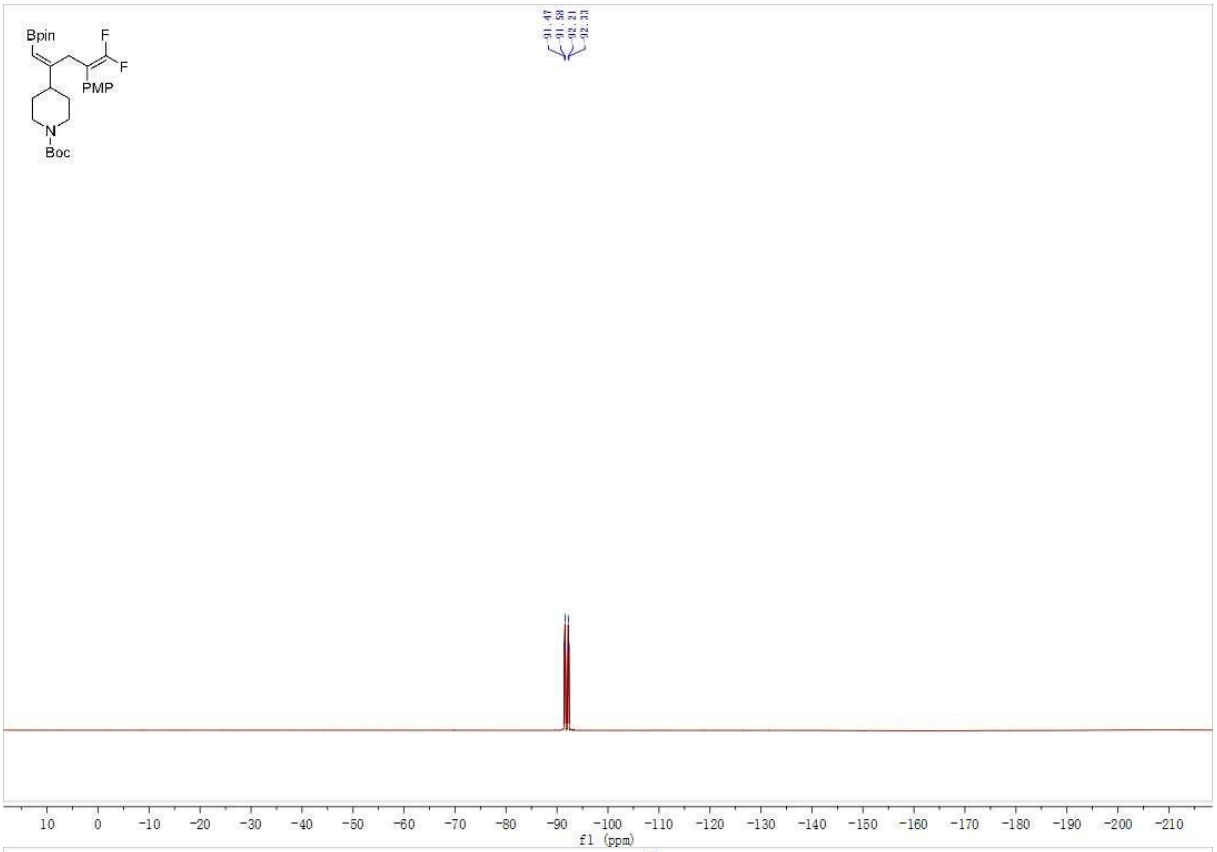
tert-butyl (E)-4-(5,5-difluoro-4-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,4-dien-2-yl)piperidine-1-carboxylate (3h)

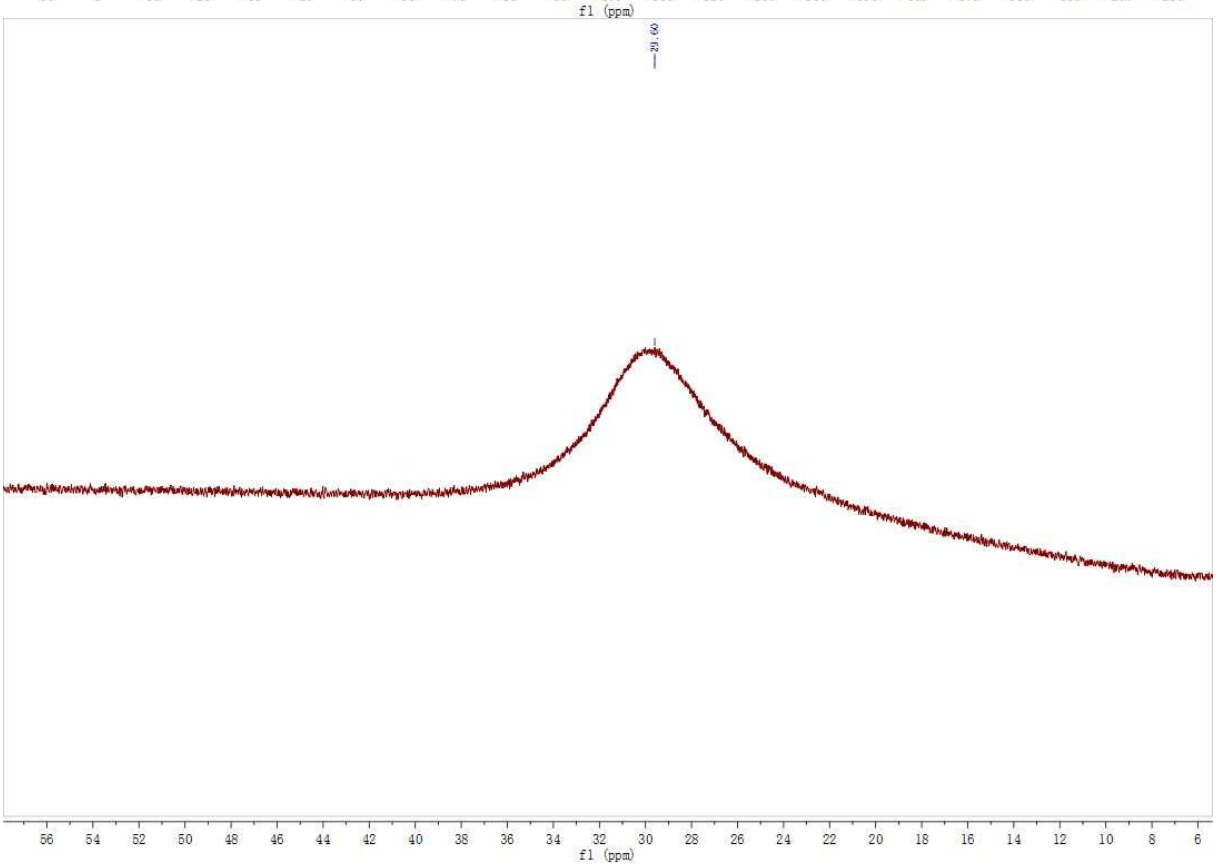


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (10:1) as white solid (71.8 mg, 69 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 5.15 (s, 1H), 4.20 - 4.00 (m, 2H), 3.78 (s, 3H), 3.65 (s, 2H), 2.64 - 2.54 (m, 2H), 2.02 - 1.92 (m, 1H), 1.56 - 1.48 (m, 2H), 1.44 (s, 9H), 1.34 - 1.20 (m, 14 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.95, 158.63, 154.82, 154.15 (dd, *J* = 289.6, 286.3 Hz), 129.82, 125.25, 113.67, 113.53, 90.71 (dd, *J* = 20.9, 13.6 Hz), 82.95, 79.33, 55.19, 44.39, 41.96, 31.97, 31.43, 28.45, 24.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.52 (d, *J* = 44.2 Hz), -92.27 (d, *J* = 44.2 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.60. HRMS (ESI^+): Calcd for $C_{28}H_{40}BF_2NO_5$ $[H]^+$: 520.3046, Found: 520.3057.

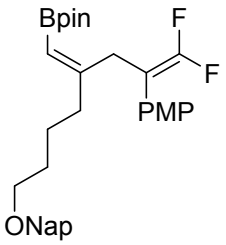

Bpin
F
F
PMP
N
Boc
f1 (ppm)


Bpin
F
F
PMP
N
Boc
f1 (ppm)

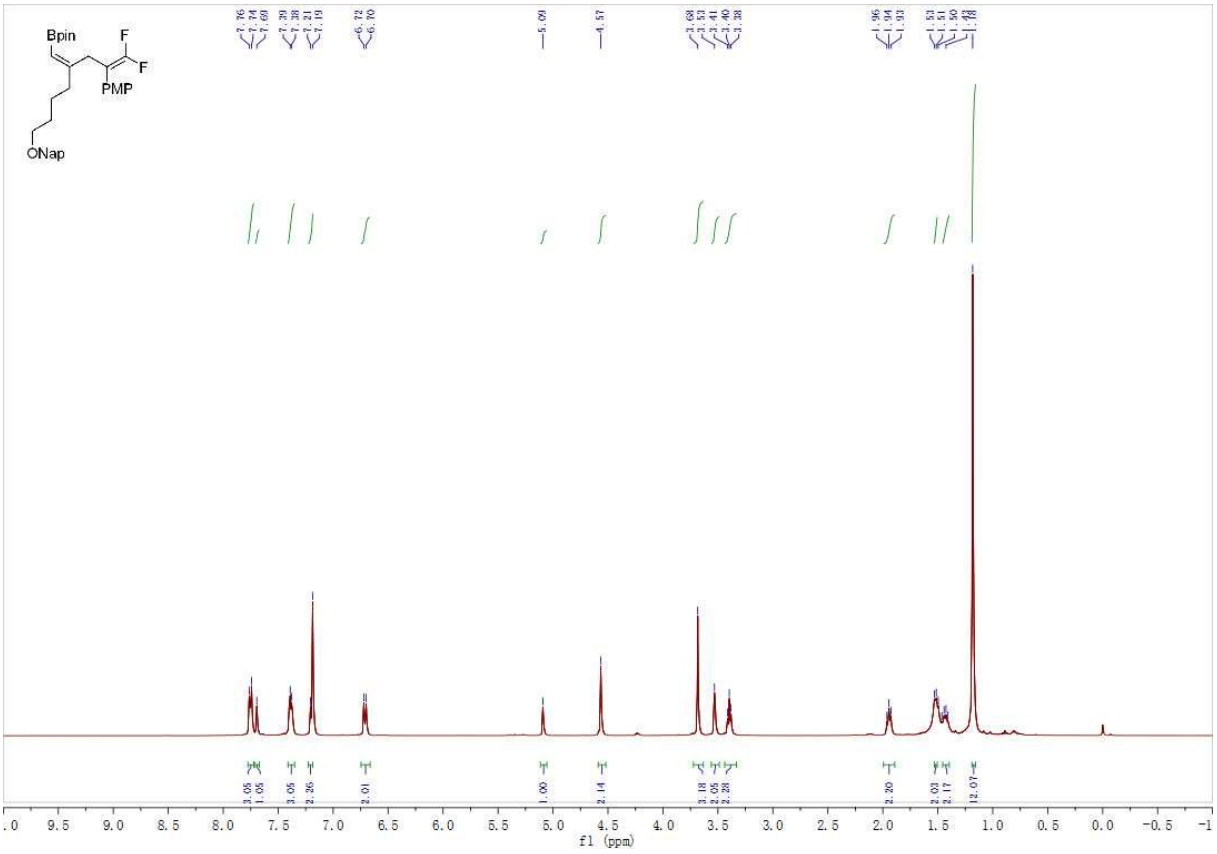

Bpin
F
F
PMP
N
Boc
-91.47
-91.58
-92.21
-92.33
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

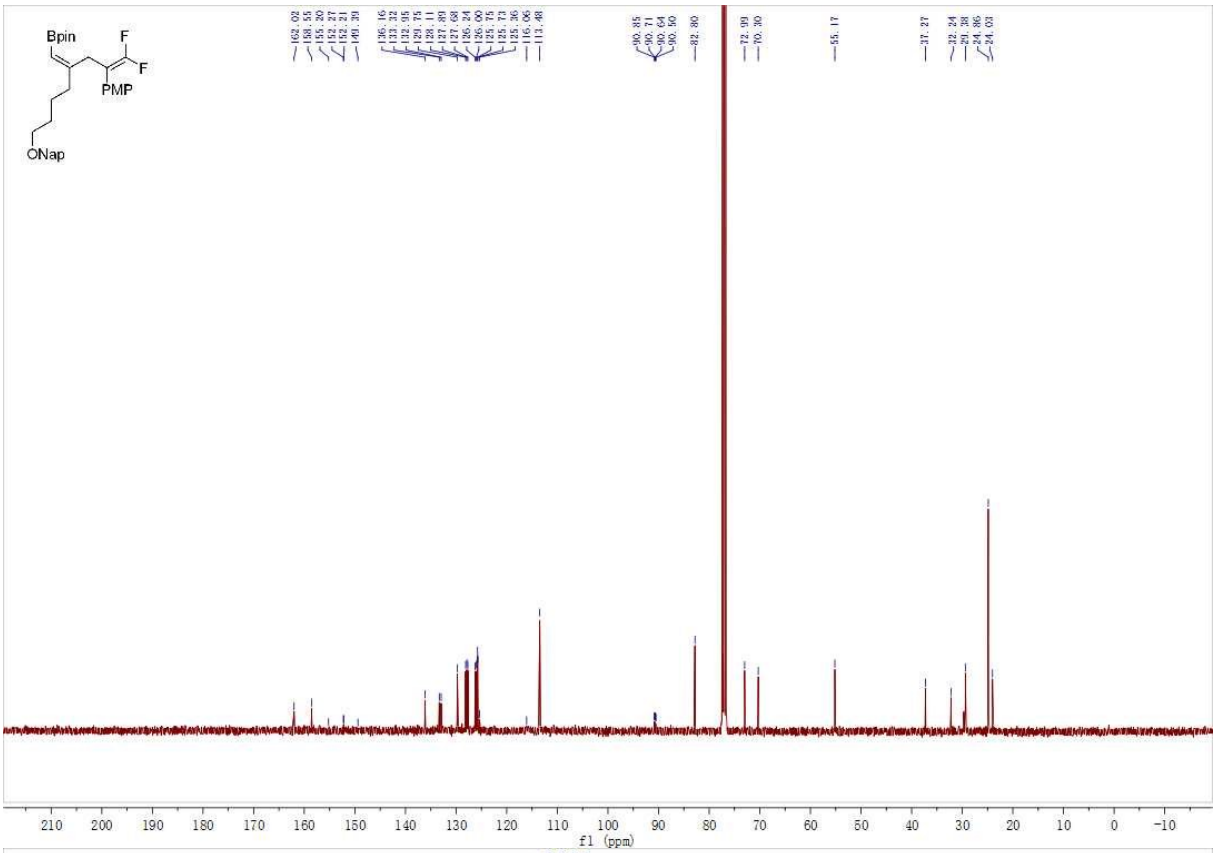

29.60
56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6
f1 (ppm)

(Z)-2-(2-(3,3-difluoro-2-(4-methoxyphenyl)allyl)-6-(naphthalen-2-ylmethoxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (15:1) as thick oil (70.3 mg, 64 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 - 7.73 (m, 3H), 7.69 (s, 1H), 7.41 - 7.36 (m, 3H), 7.20 (d, *J* = 7.7 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 5.09 (s, 1H), 4.57 (d, *J* = 7.4 Hz, 2H), 3.68 (s, 3H), 3.53 (s, 2H), 3.40 (t, *J* = 6.2 Hz, 2H), 1.94 (t, *J* = 7.2 Hz, 2H), 1.57 - 1.48 (m, 2H), 1.46 - 1.38 (m, 2H), 1.18 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.02, 158.55, 152.27 (dd, *J* = 295.5, 288.8 Hz), 136.16, 133.32, 132.95, 129.75, 128.11, 127.89, 127.68, 126.24, 126.00, 125.75, 125.73, 125.36, 116.06, 113.48, 90.68 (dd, *J* = 21.0, 13.6 Hz), 82.80, 72.99, 70.30, 55.17, 37.27, 32.24, 29.38, 24.86, 24.03. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.96 (d, *J* = 44.5 Hz), -92.29 (d, *J* = 44.5 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.02. HRMS (ESI^+): Calcd for $C_{33}H_{39}BF_2O_4$ $[H]^+$: 549.2988, Found: 549.2990.




Bpin
F
F
PMP
ONap
162.02
158.55
153.20
132.27
129.21
136.16
133.32
132.95
129.75
128.11
127.80
127.68
126.24
126.00
125.75
125.73
125.36
116.06
113.48
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90.71
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90.50
82.80
72.99
70.30
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24.68
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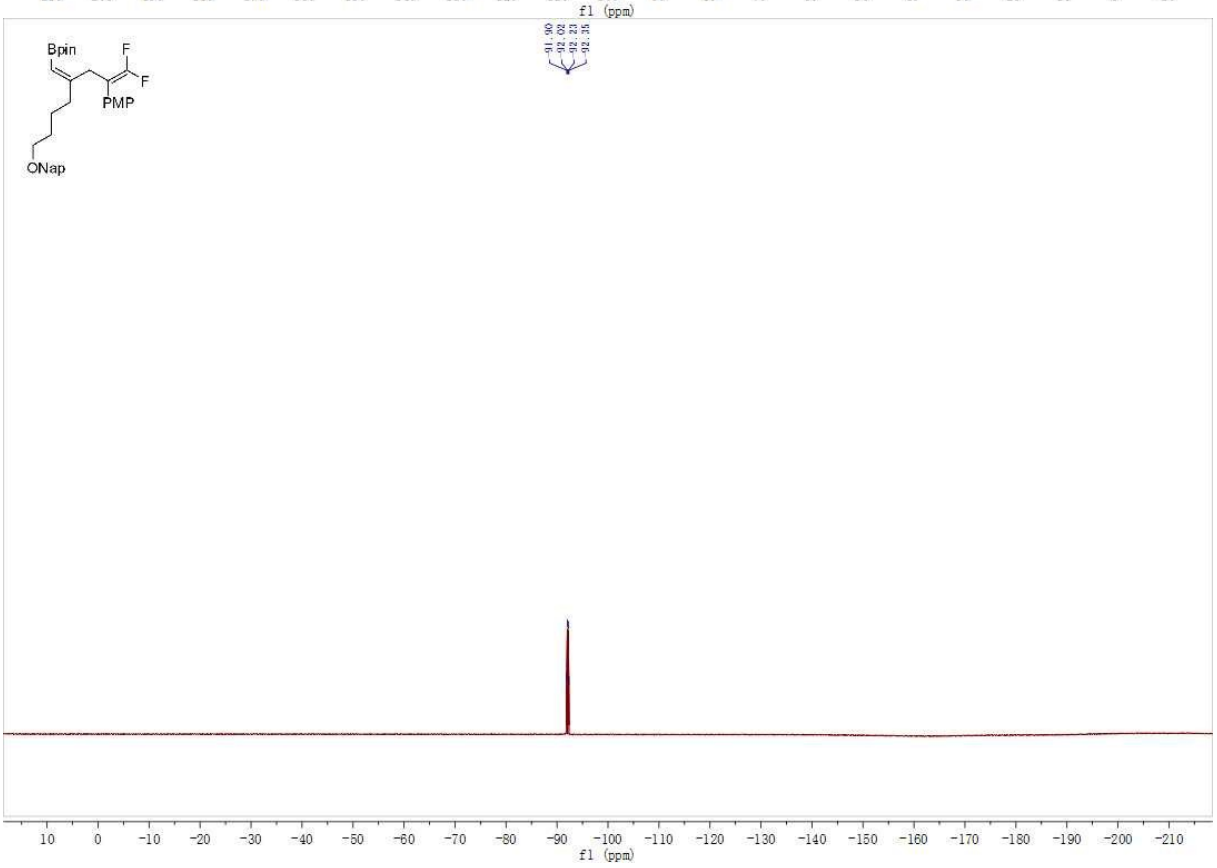
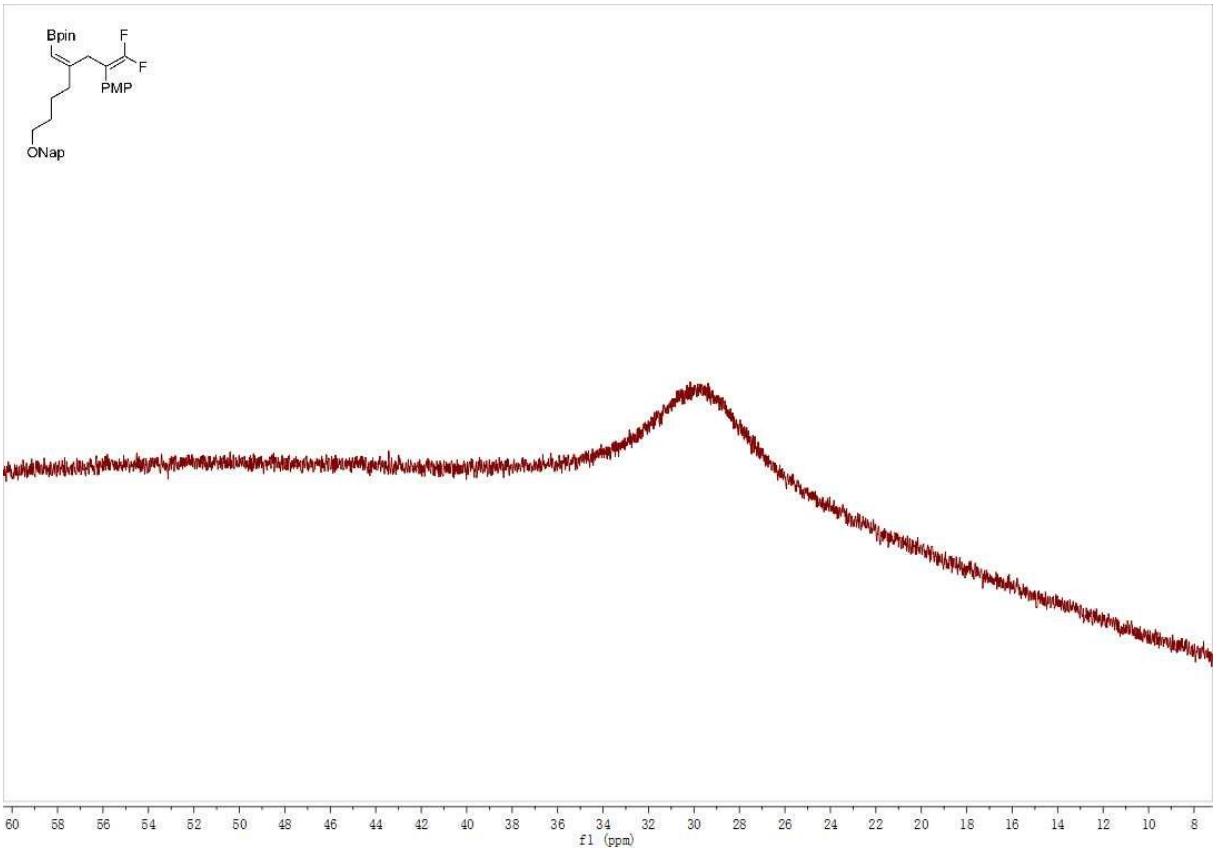
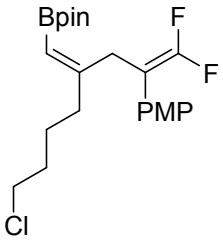
f1 (ppm)

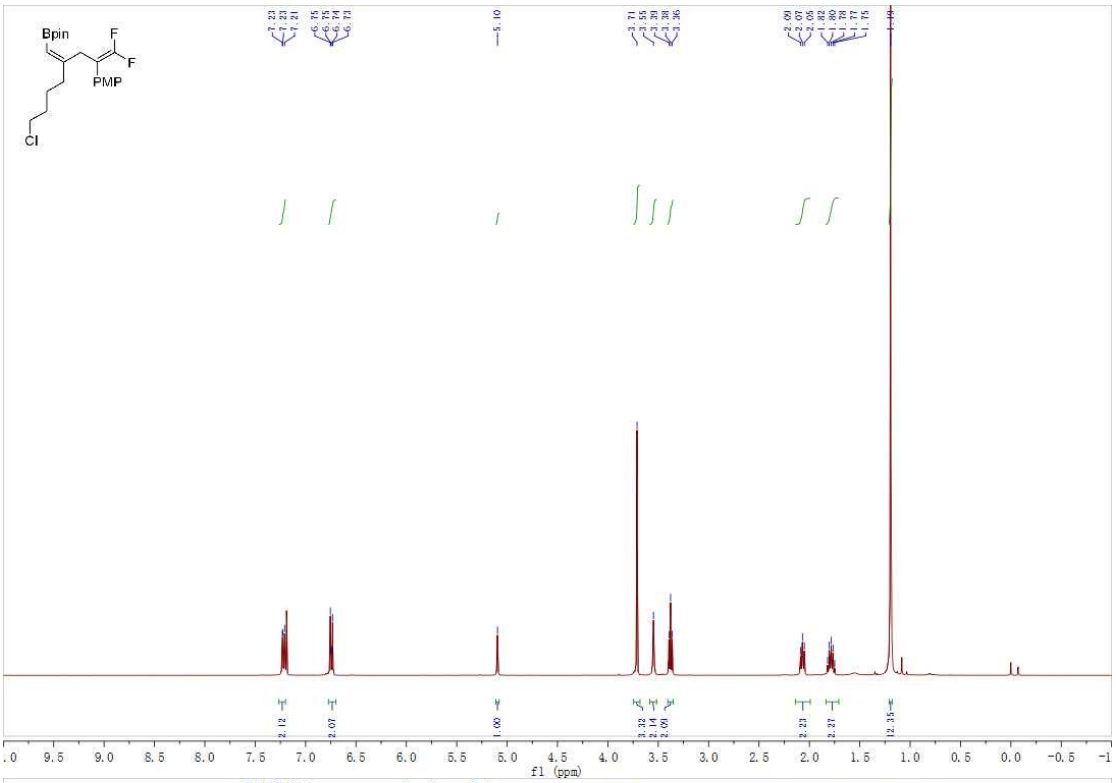

Bpin
F
F
PMP
ONap
91.90
92.02
92.23
92.35
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

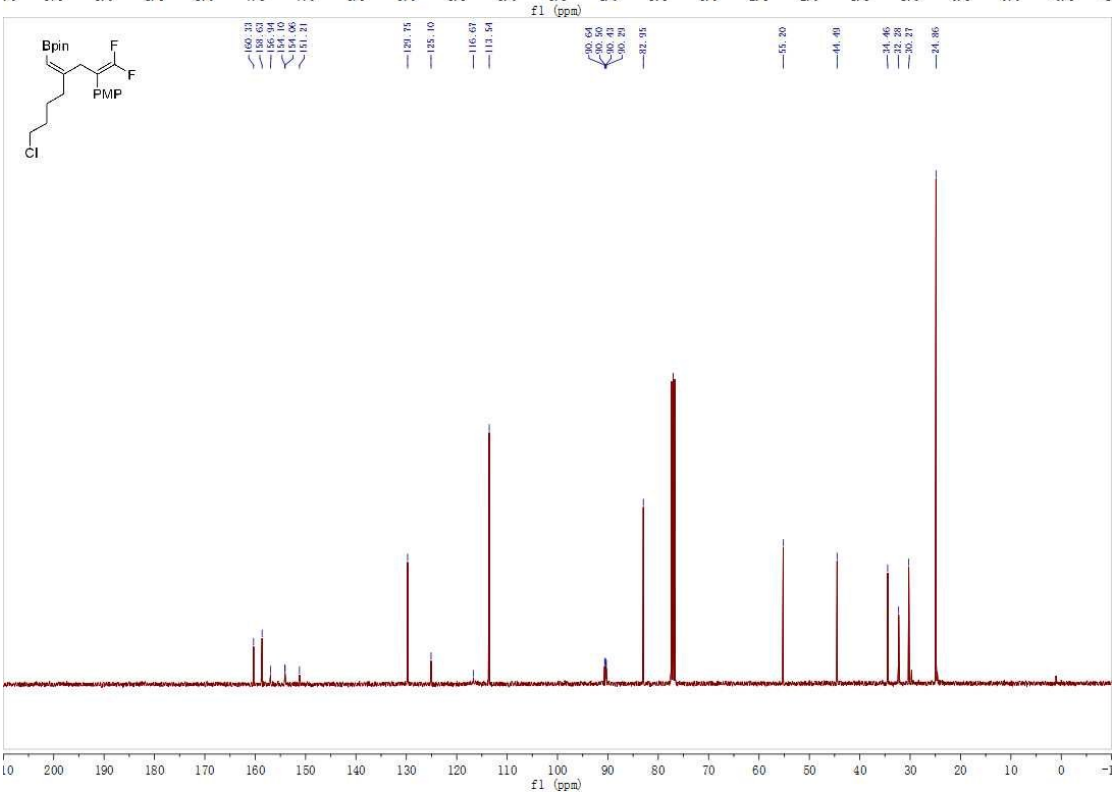


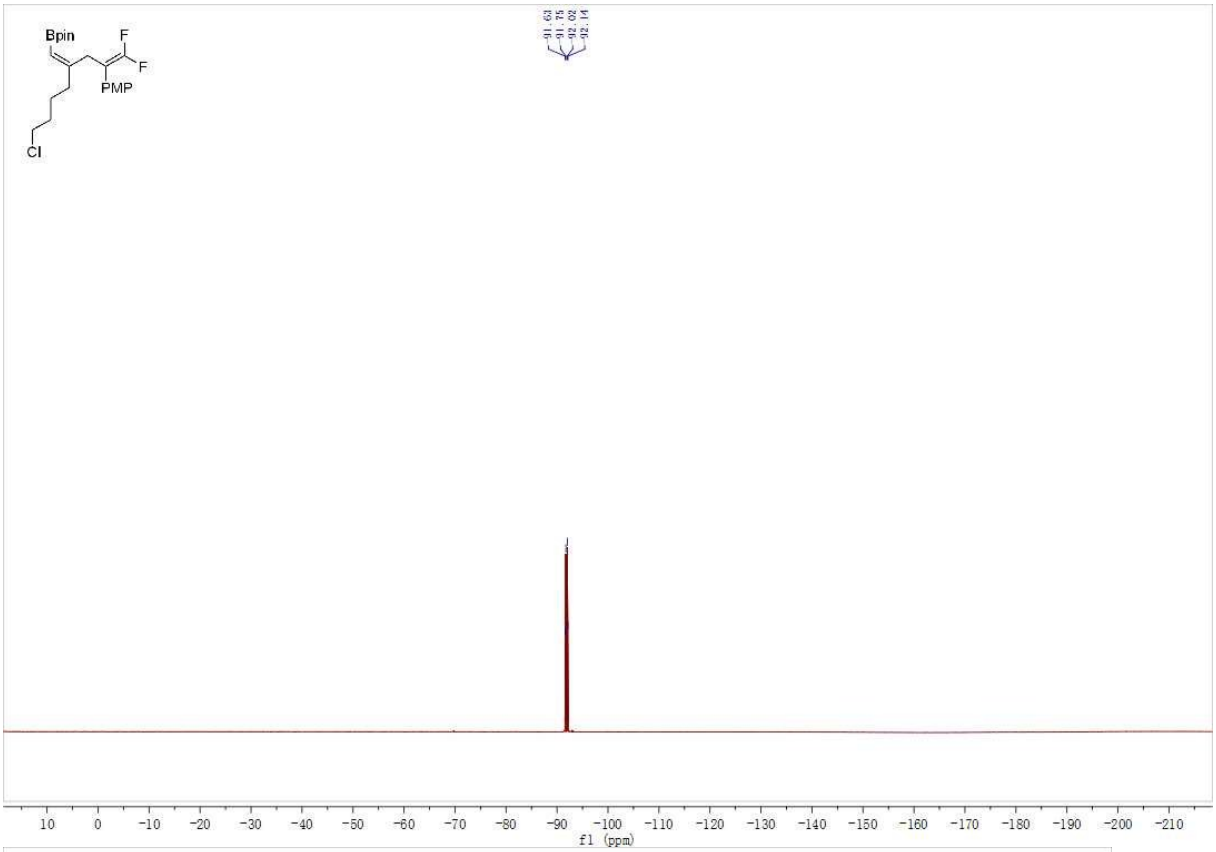
(Z)-2-(6-chloro-2-(3,3-difluoro-2-(4-methoxyphenyl)allyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (50:1) as thick oil (61.2 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.06 (m, 2H), 6.84 - 6.52 (m, 2H), 5.10 (s, 1H), 3.71 (s, 3H), 3.55 (s, 2H), 3.38 (t, *J* = 6.6 Hz, 2H), 2.07 (t, *J* = 7.5 Hz, 2H), 1.91 - 1.66 (m, 2H), 1.19 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.33, 158.63, 154.08 (dd, *J* = 289.9, 286.3 Hz), 129.75, 125.10, 116.67, 113.54, 90.47 (dd, *J* = 21.0, 13.8 Hz), 82.95, 55.20, 44.49, 34.46, 32.28, 30.27, 29.72, 24.86. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.69 (d, *J* = 44.2 Hz), -92.08 (d, *J* = 44.2 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.72. HRMS (ESI^+): Calcd for $C_{22}H_{30}BClF_2O_3$ $[H]^+$: 427.2023, Found: 427.2069.


Bpin
F
F
PMP
Cl
f1 (ppm)


Bpin
F
F
PMP
Cl
f1 (ppm)


Bpin
F
F
PMP
Cl
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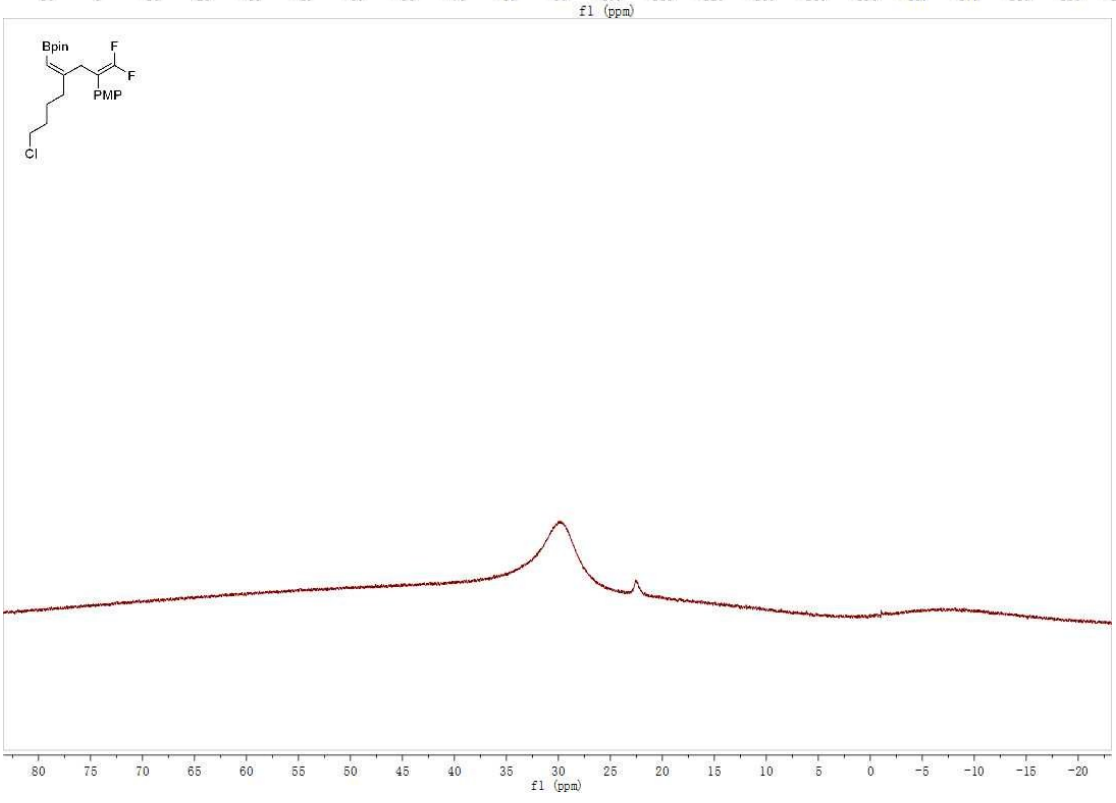
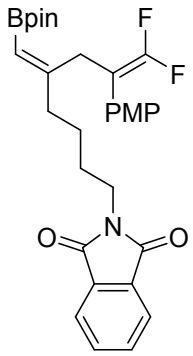
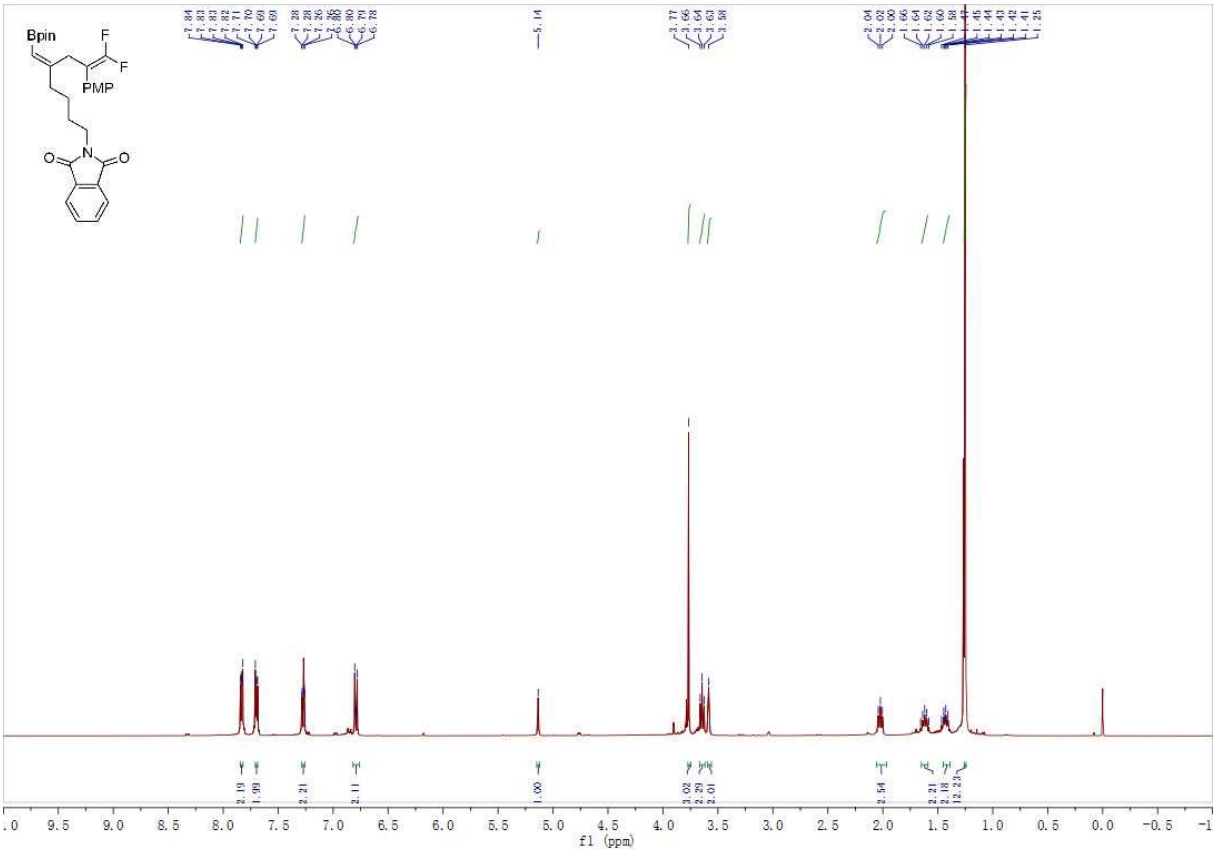
-91.75
-92.02
-92.14
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

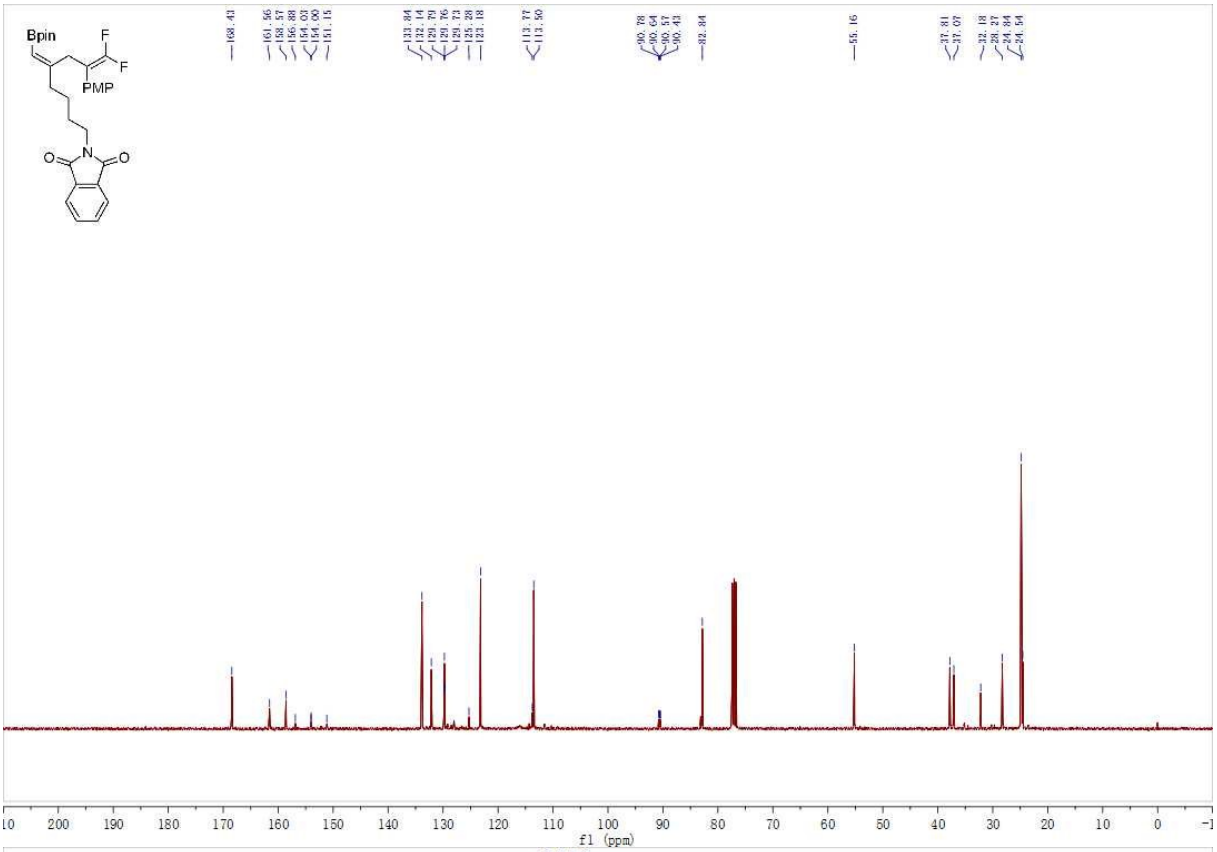

Bpin
F
F
PMP
Cl
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20
f1 (ppm)

(Z)-2-(8,8-difluoro-7-(4-methoxyphenyl)-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)oct-7-en-1-yl)isoindoline-1,3-dione (3k)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (10:1) as white solid (65 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.81 (m, 2H), 7.73 - 7.67 (m, 2H), 7.37 - 7.23 (m, 2H), 6.84 - 6.70 (m, 2H), 5.14 (s, 1H), 3.77 (s, 3H), 3.64 (t, *J* = 7.1 Hz, 2H), 3.58 (s, 2H), 2.09 - 1.93 (m, 2H), 1.67 - 1.57 (m, 2H), 1.49 - 1.37 (m, 2H), 1.25 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.43, 161.56, 158.57, 154.01 (dd, *J* = 289.7, 286.3 Hz), 133.84, 132.14, 129.76, 125.28, 123.18, 113.77, 113.50, 90.61 (dd, *J* = 21.0, 13.6 Hz), 82.84, 55.16, 37.81, 37.07, 32.18, 28.27, 24.84, 24.54. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.90 (d, *J* = 44.5 Hz), -92.31 (d, *J* = 44.5 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.94. HRMS (ESI^+): Calcd for $C_{30}H_{34}BF_2NO_5$ $[H]^+$: 538.2576, Found: 538.2585.




Bpin
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PMP
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O
168.43
161.56
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156.88
154.03
154.00
151.15
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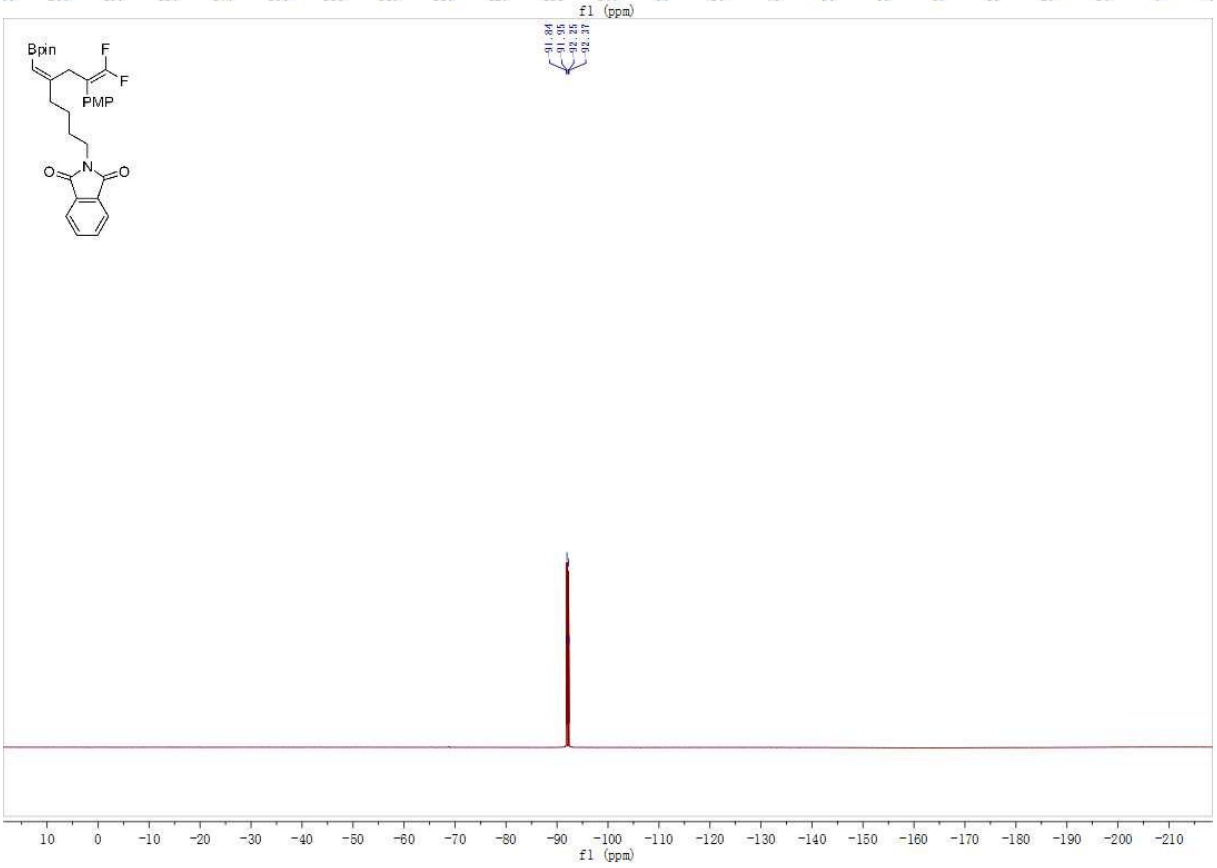
28.27
24.84
24.64
f1 (ppm)


Bpin
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F
PMP
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N
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91.95
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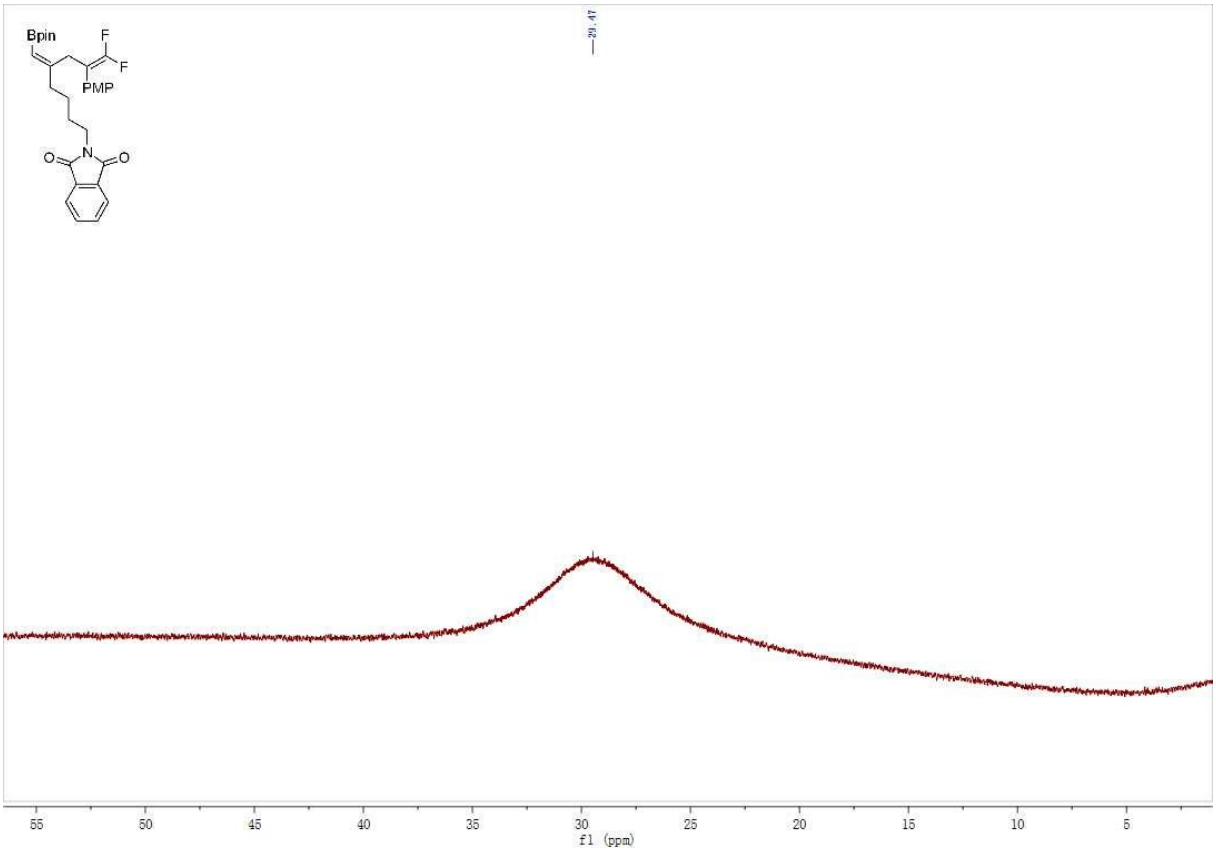
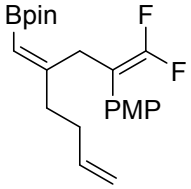
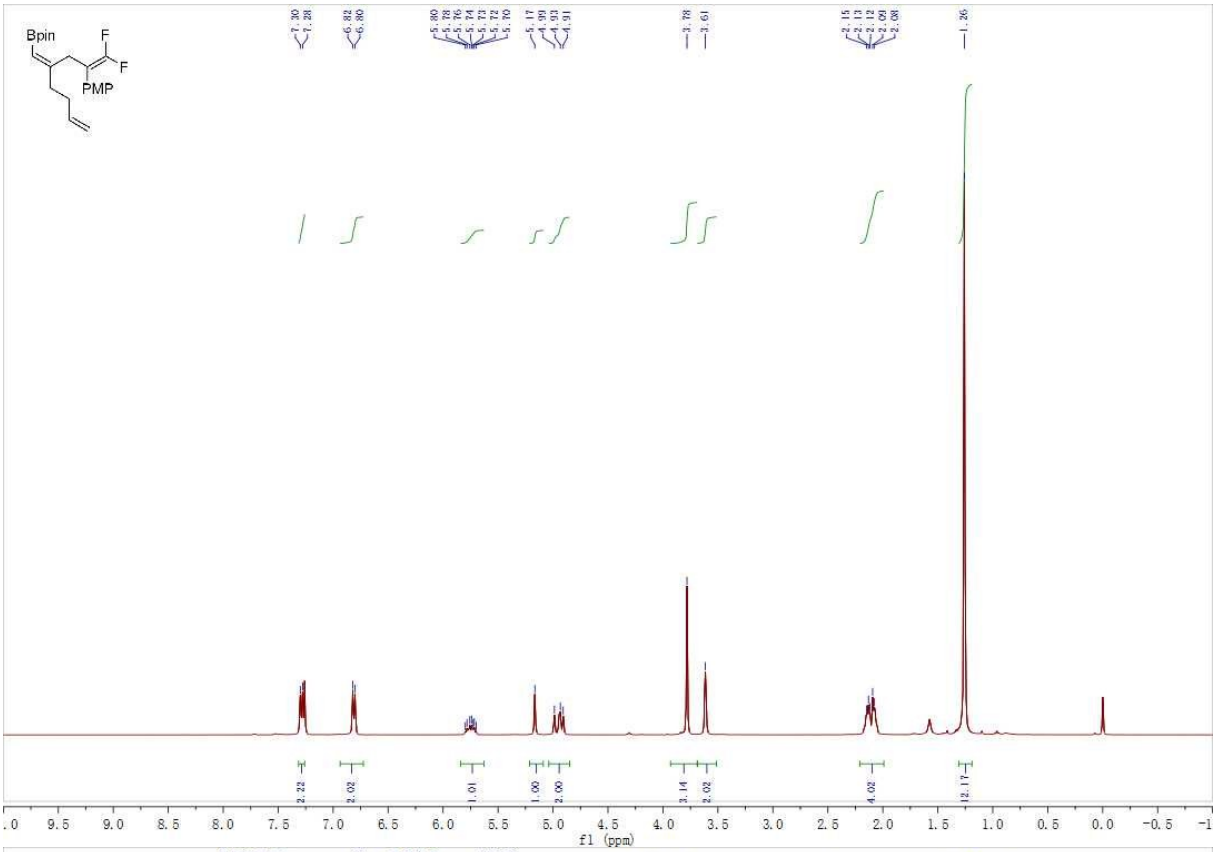
92.37
f1 (ppm)



(Z)-2-(2-(3,3-difluoro-2-(4-methoxyphenyl)allyl)hexa-1,5-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (65.7 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 5.94 - 5.48 (m, 1H), 5.17 (s, 1H), 5.05 - 4.79 (m, 2H), 3.78 (s, 3H), 3.61 (s, 2H), 2.17 - 2.04 (m, 4H), 1.26 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.40, 158.59, 154.07 (dd, *J* = 289.6, 286.2 Hz), 138.12, 129.76 (t, *J* = 3.2 Hz), 125.33, 114.66, 113.97, 113.50, 90.60 (dd, *J* = 21.1, 13.6 Hz), 82.83, 55.18, 36.83, 32.39, 31.64, 24.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.90 (d, *J* = 44.4 Hz), -92.29 (d, *J* = 44.4 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.67. HRMS (ESI^+): Calcd for $C_{22}H_{29}BF_2O_3$ $[H]^+$: 391.2256, Found: 391.2260.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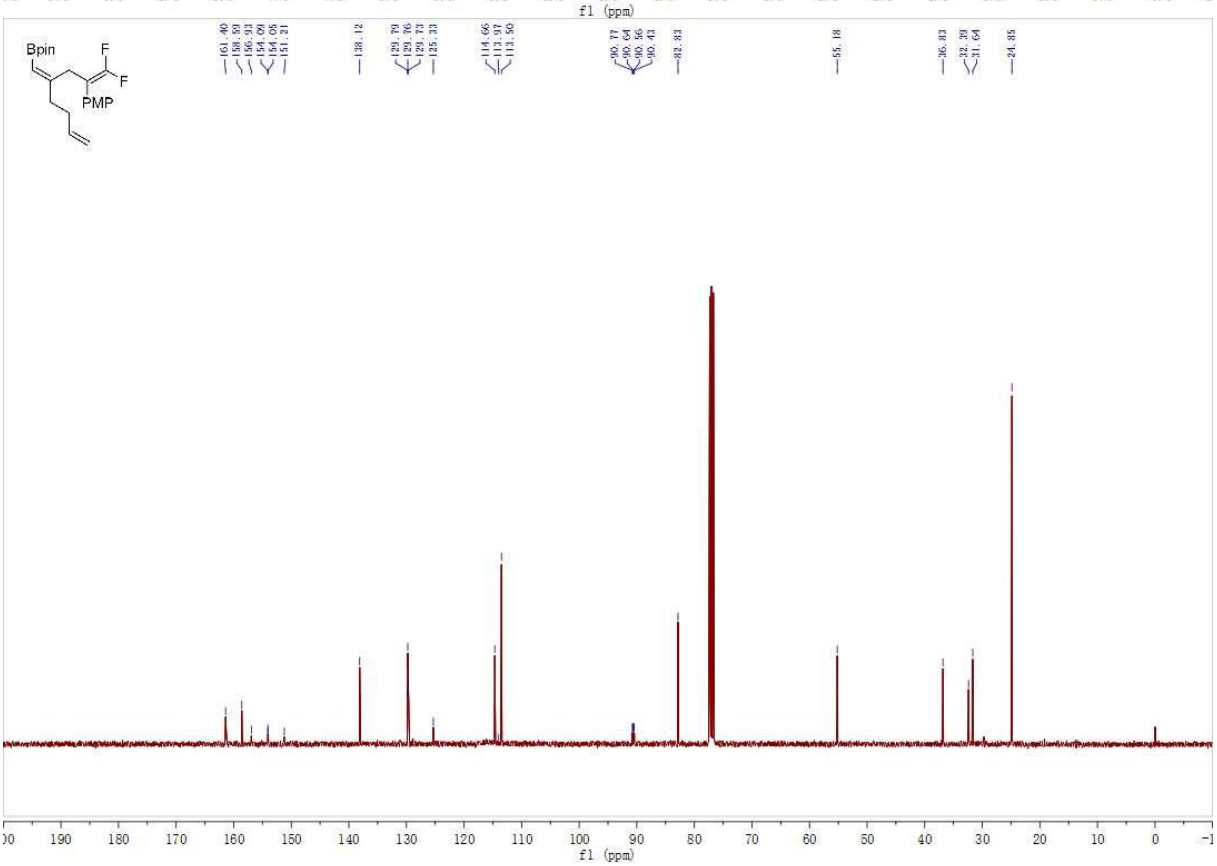
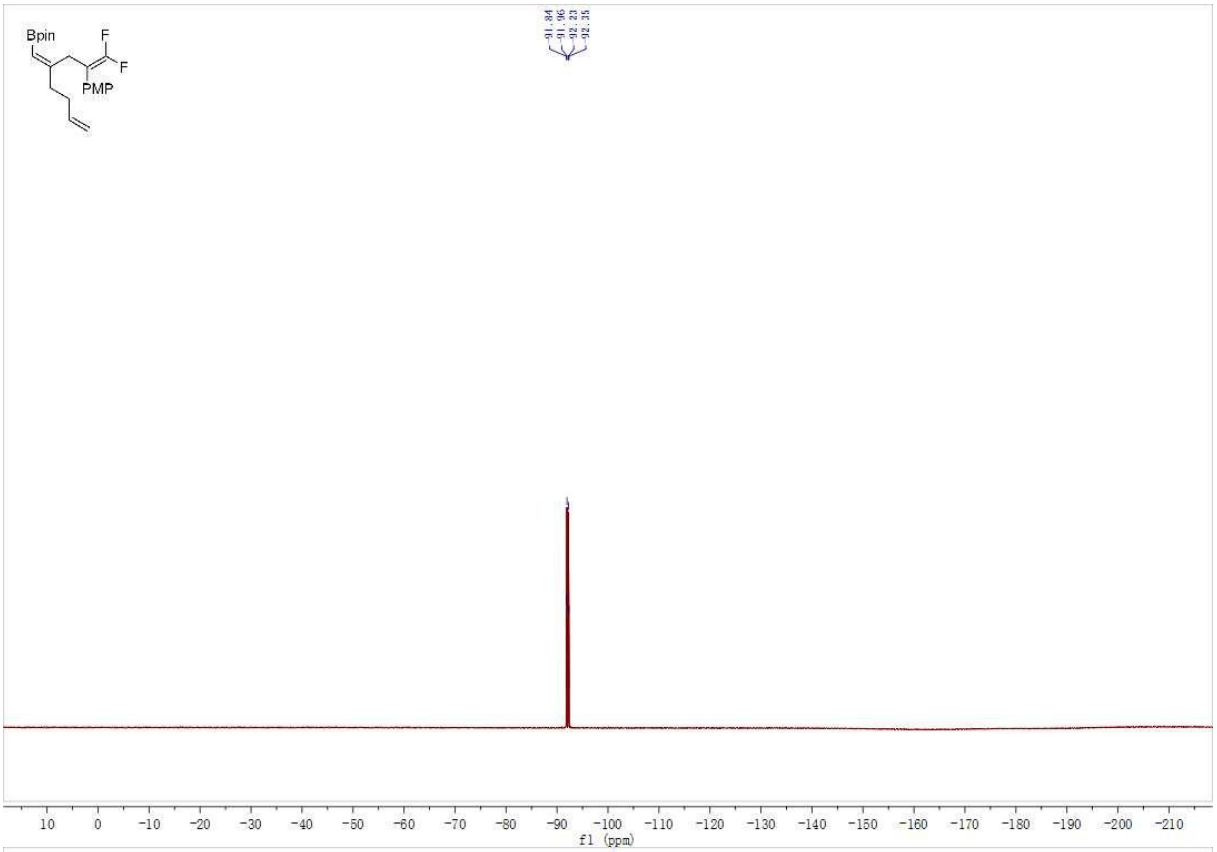
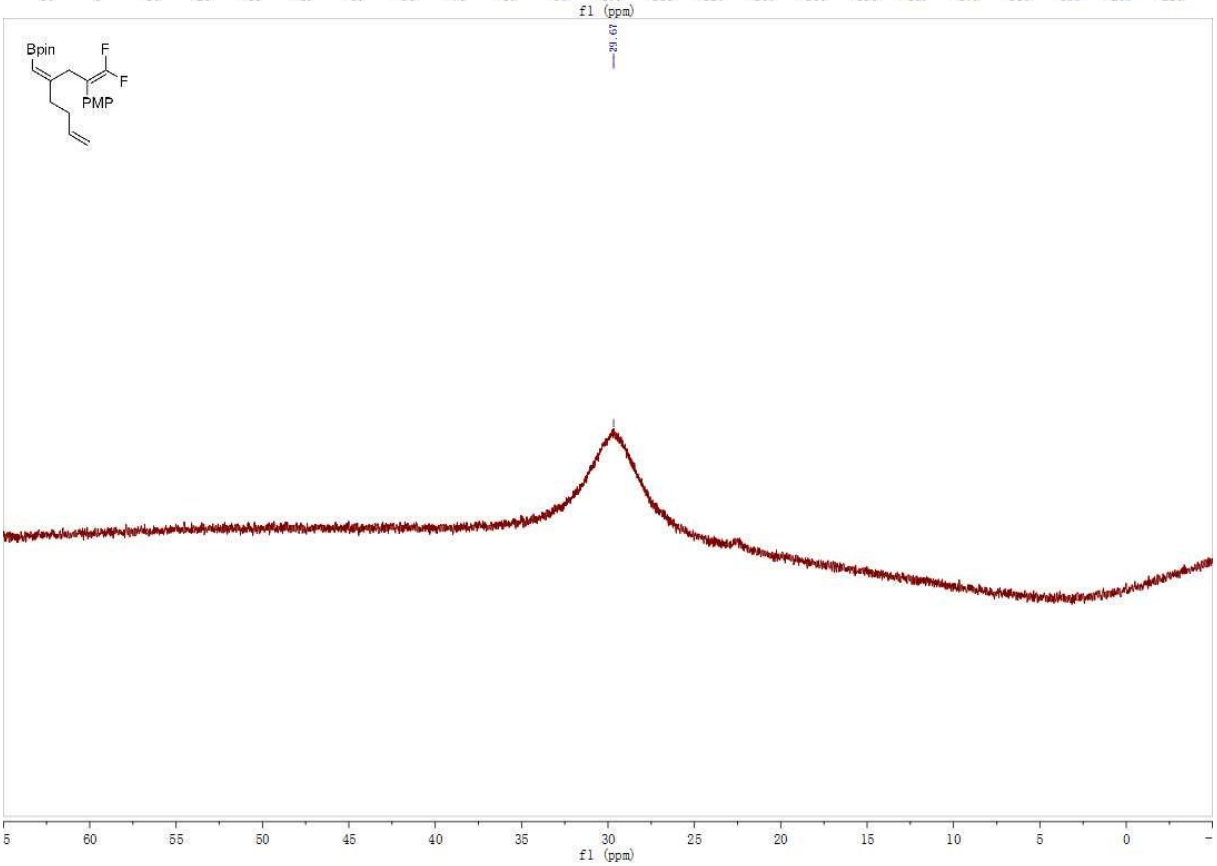
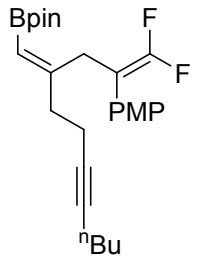
F
PMP
f1 (ppm)


Bpin
F
F
PMP
f1 (ppm)

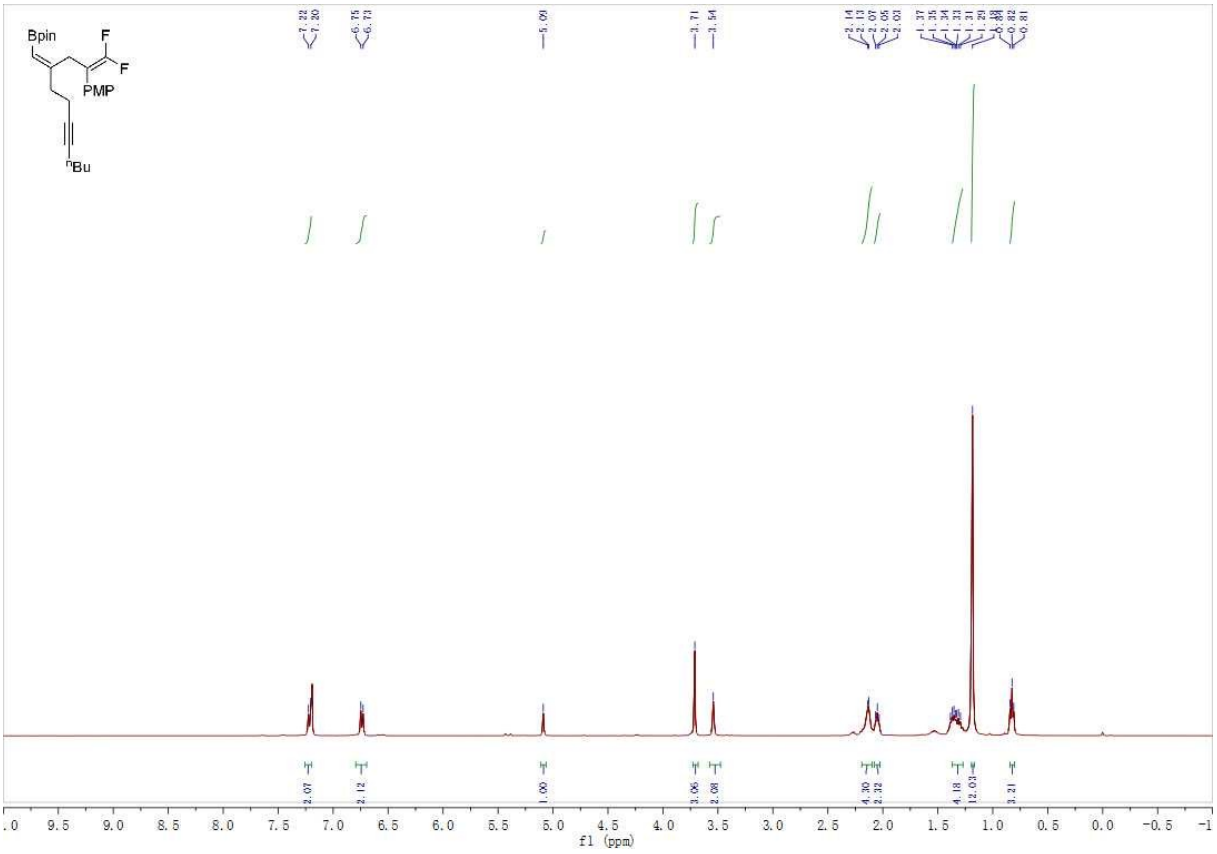

Bpin
F
F
PMP
-91.84
-91.96
-92.23
-92.35
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

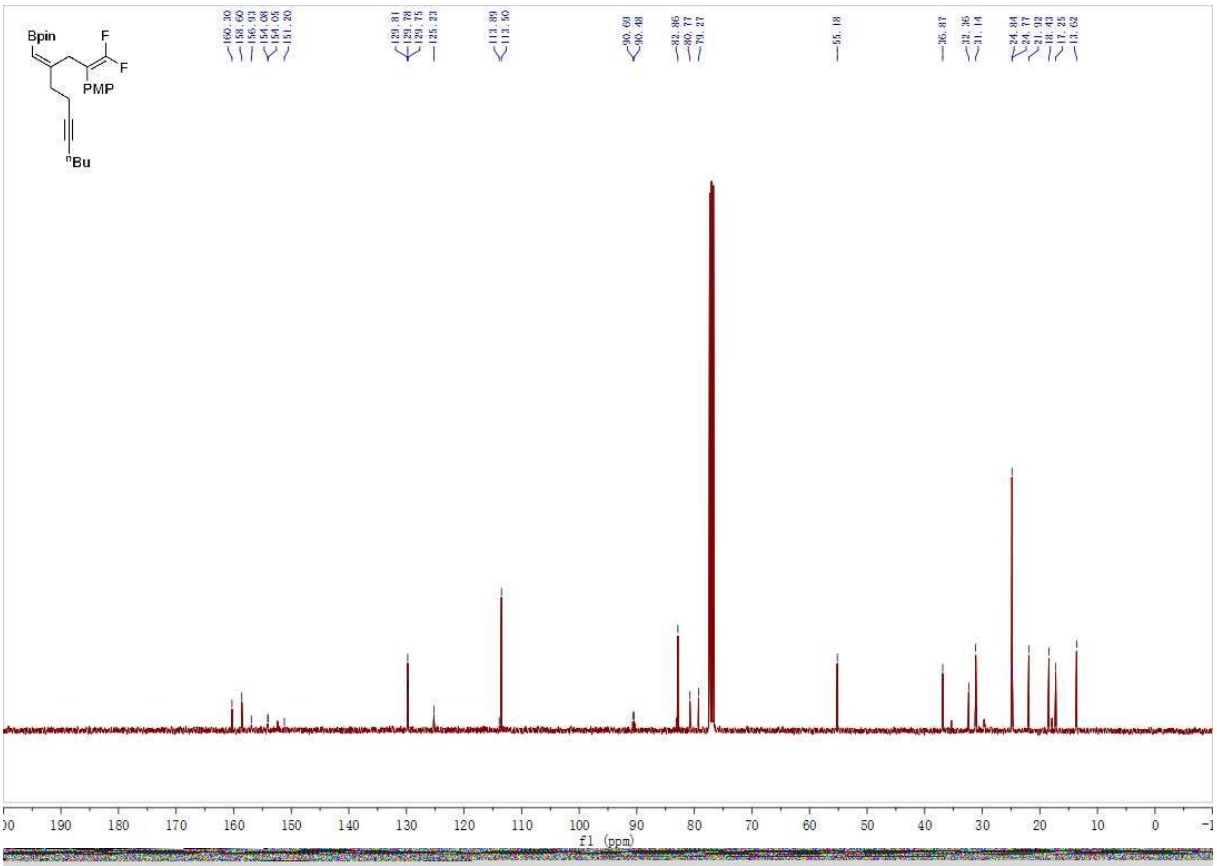

Bpin
F
F
PMP
29.67
65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

(Z)-2-(2-(3,3-difluoro-2-(4-methoxyphenyl)allyl)dec-1-en-5-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (76.6 mg, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.9 Hz, 2H), 6.74 (d, *J* = 8.1 Hz, 2H), 5.09 (s, 1H), 3.71 (s, 3H), 3.54 (s, 2H), 2.21 - 2.08 (m, 4H), 2.05 (t, *J* = 6.4 Hz, 2H), 1.42 - 1.24 (m, 4H), 1.18 (s, 12H), 0.83 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.30, 158.60, 154.07 (dd, *J* = 289.7, 286.9 Hz), 129.78, 125.23, 113.89, 113.50, 90.58 (d, *J* = 20.9 Hz), 82.86, 80.77, 79.27, 55.18, 36.87, 32.36, 31.14, 24.84, 21.92, 18.43, 17.25, 13.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.69 (d, *J* = 44.2 Hz), -92.18 (d, *J* = 44.2 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.54. HRMS (ESI^{+}): Calcd for $C_{26}H_{35}BF_2O_3$ [H]$^{+}$: 445.2726, Found: 445.2727.




Bpin
F
F
PMP
nBu
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158.60
156.93
154.08
153.65
151.20
129.81
129.78
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125.23
113.89
113.50
90.69
90.48
82.86
80.77
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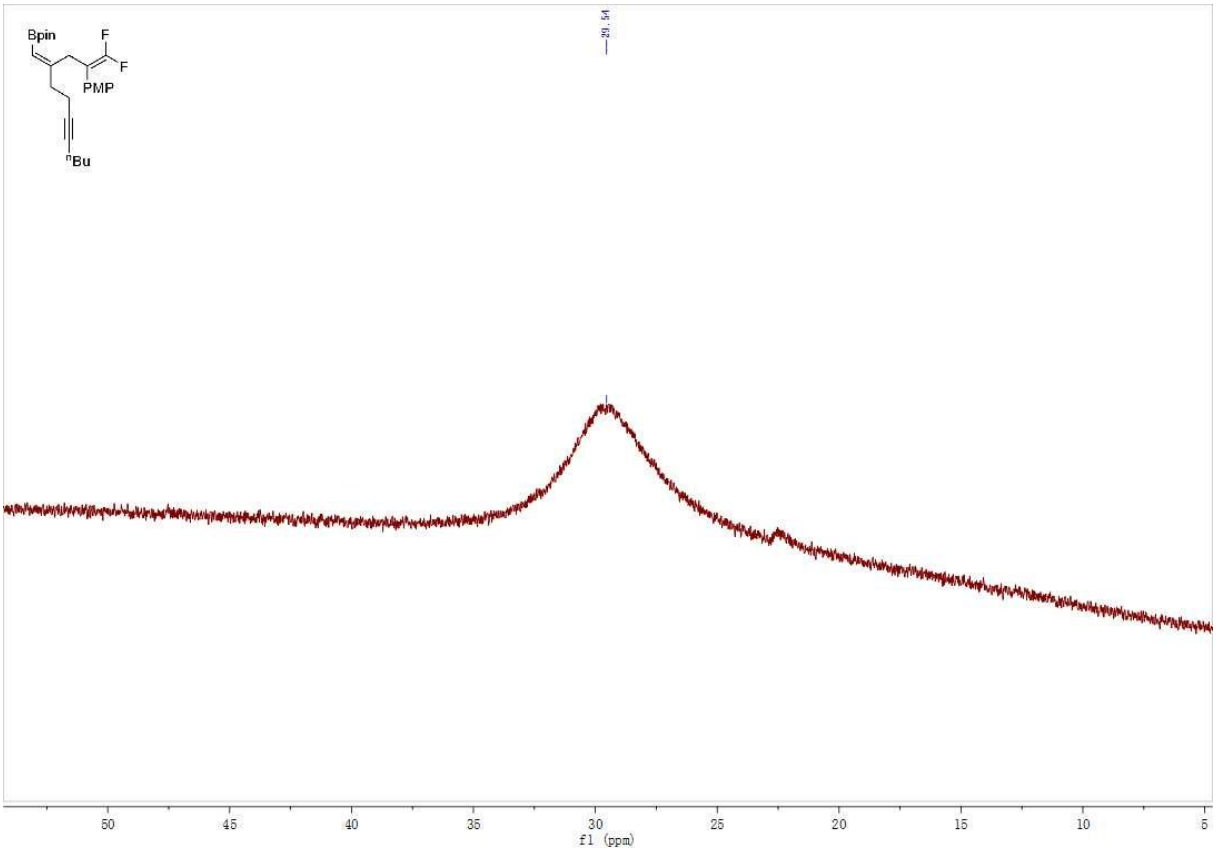
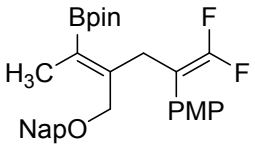
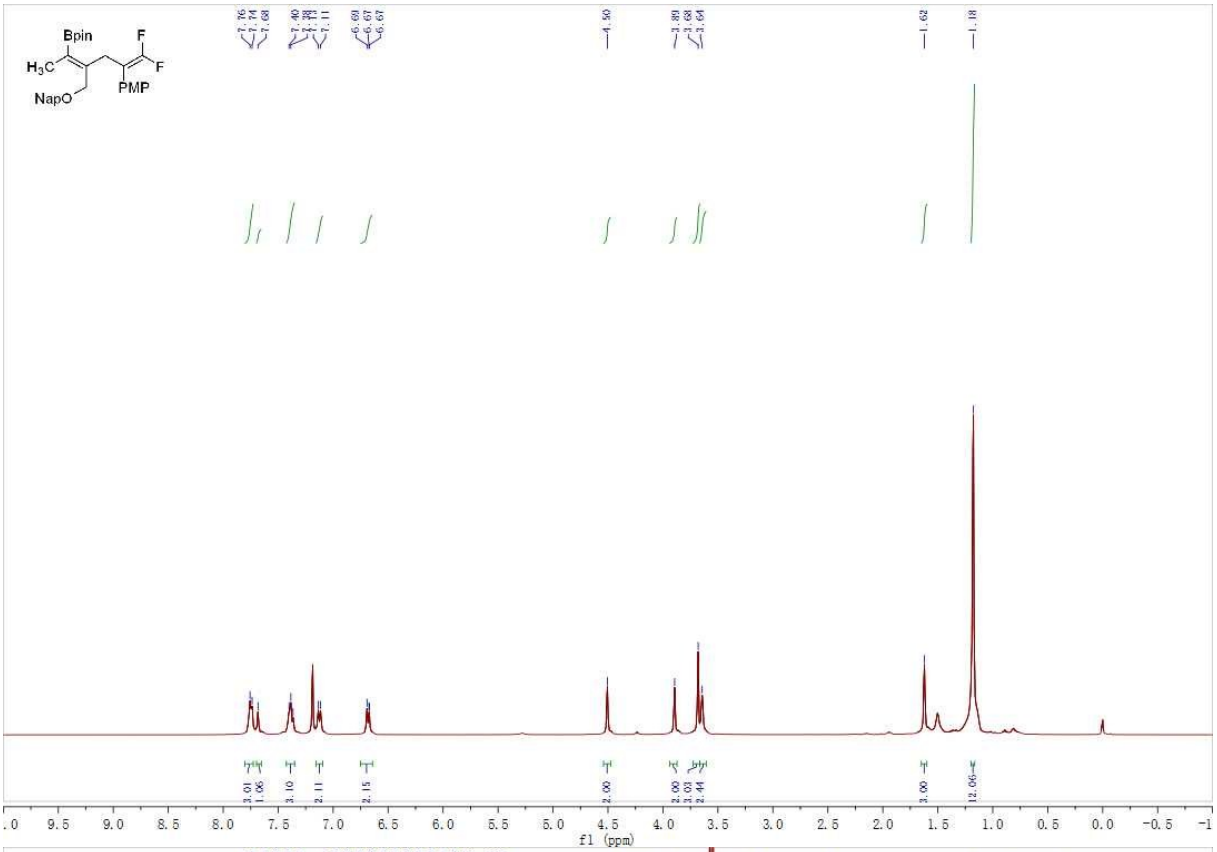
21.92
18.43
13.75
13.62
f1 (ppm)



(Z)-2-(6,6-difluoro-5-(4-methoxyphenyl)-3-((naphthalen-2-ylmethoxy)methyl)hexa-2,5-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (20:1) as thick oil (62.6 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 3H), 7.68 (s, 1H), 7.45 - 7.35 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.75 - 6.65 (m, 2H), 4.50 (s,2H), 3.89 (s, 2H), 3.89 (s, 3H), 3.68 (s, 2H), 1.62 (s, 3H), 1.18 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.44, 153.92 (dd, *J* = 286.0 62, 289.062 Hz), 146.89, 136.00, 133.30, 132.96, 129.92, 128.02, 127.90, 127.68, 126.40, 125.98, 125.91, 125.83, 125.73, 114.53, 113.41, 90.91 (dd, *J* = 15.3, 13.1 Hz), 83.16, 72.64, 67.50, 55.16, 31.50, 24.82, 16.57. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.69 (s). ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.47. HRMS (ESI^+): Calcd for $C_{31}H_{35}BF_2O_4$ $[H]^+$: 521.2675, Found: 521.2701.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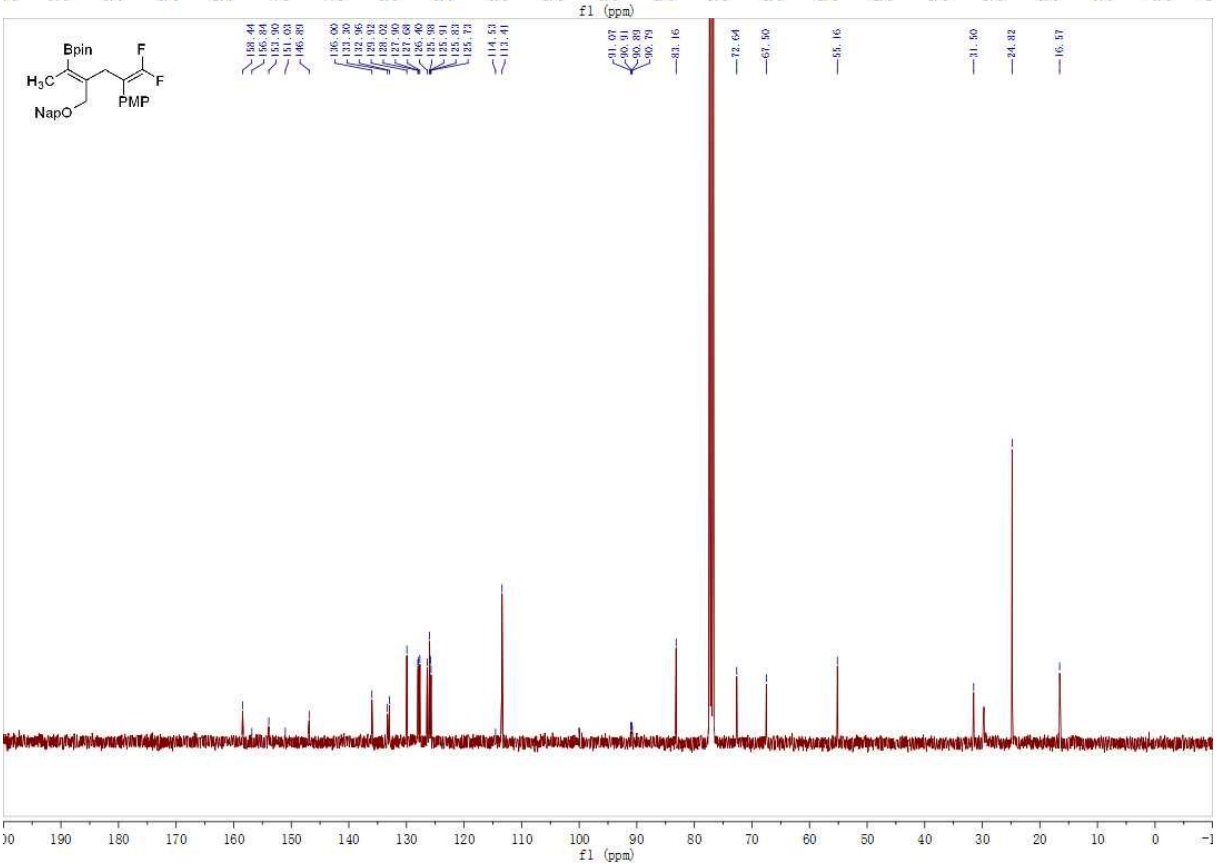
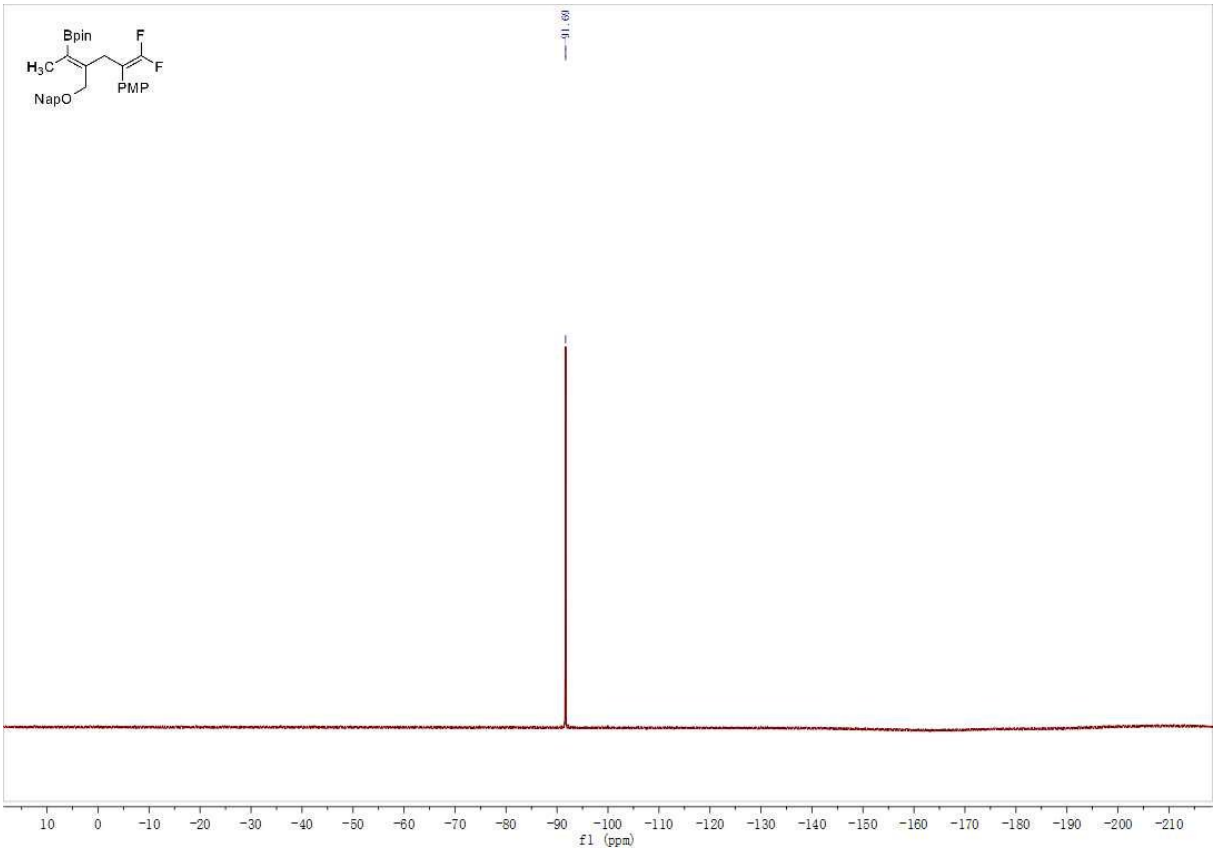
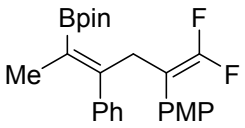
F
F
H3C
NapO
PMP
f1 (ppm)

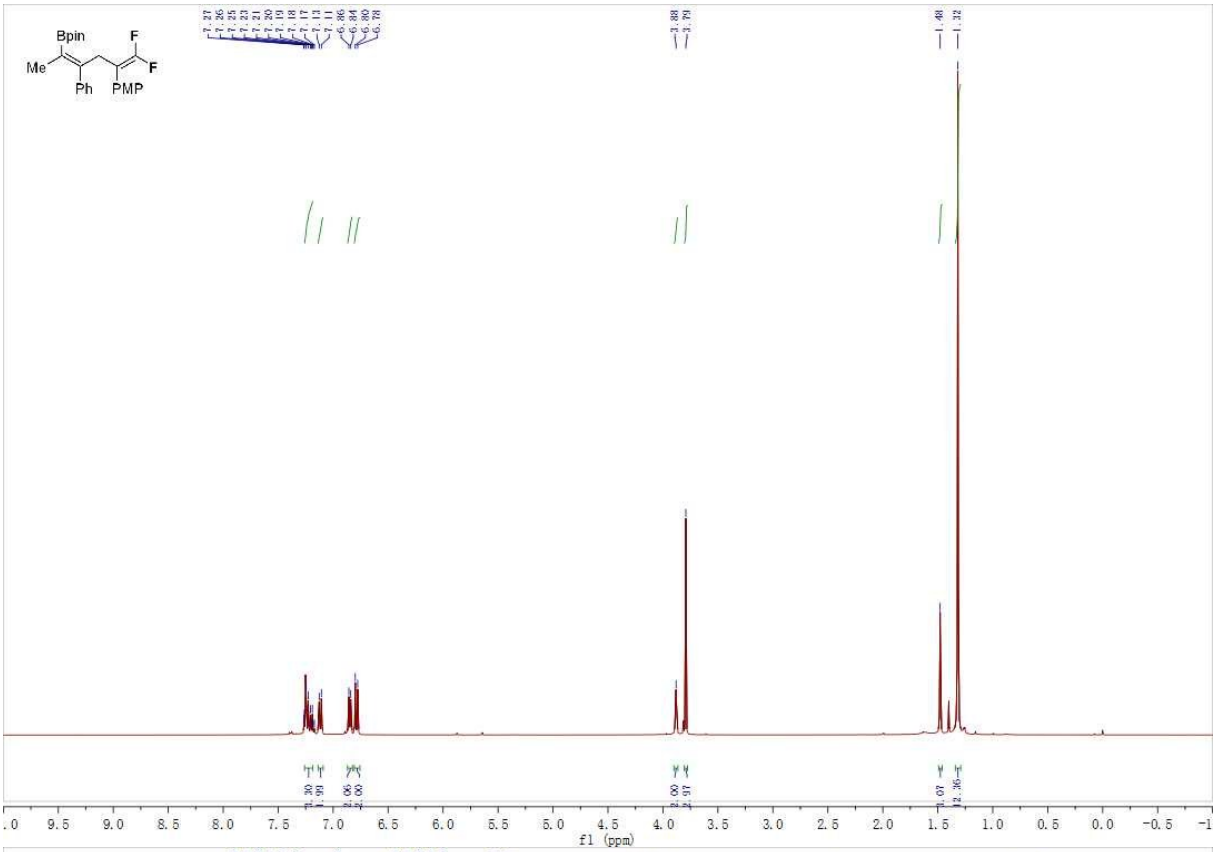

Bpin
F
F
H3C
NapO
PMP
f1 (ppm)

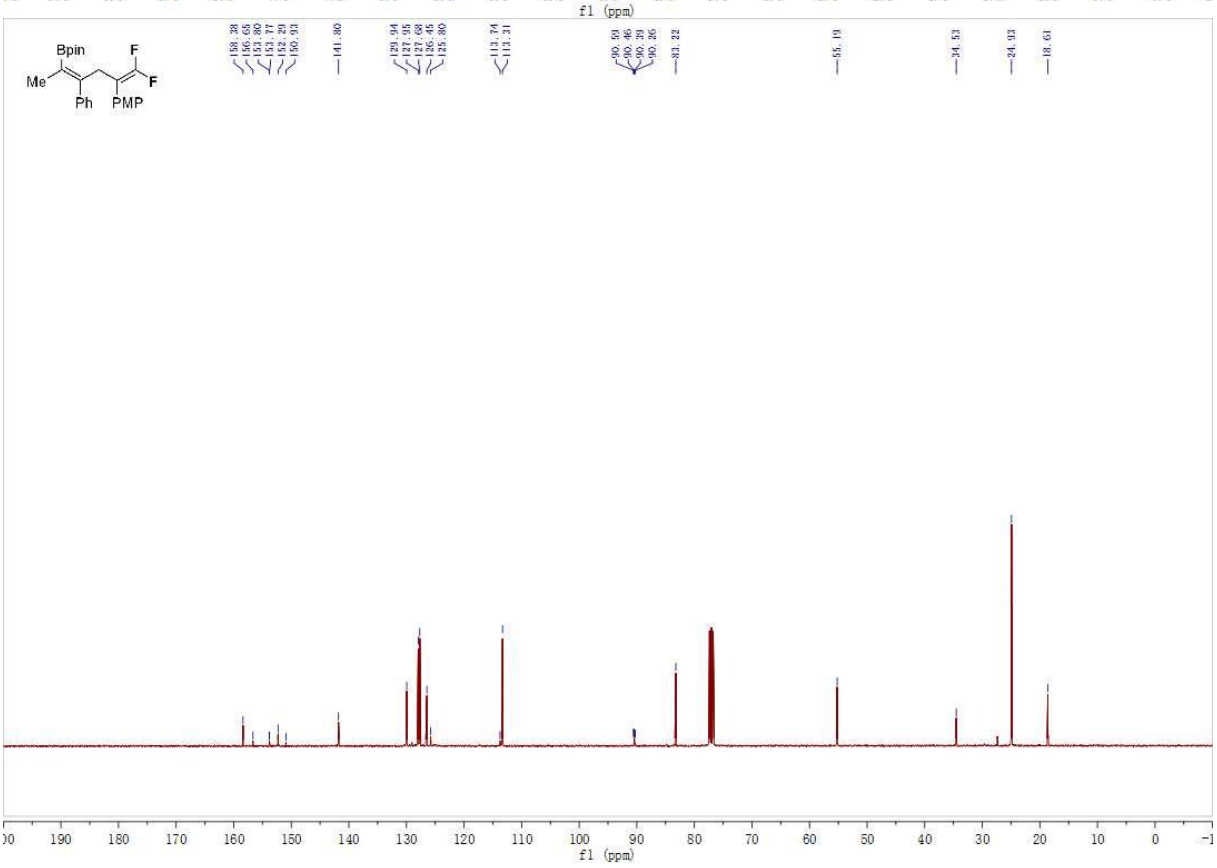


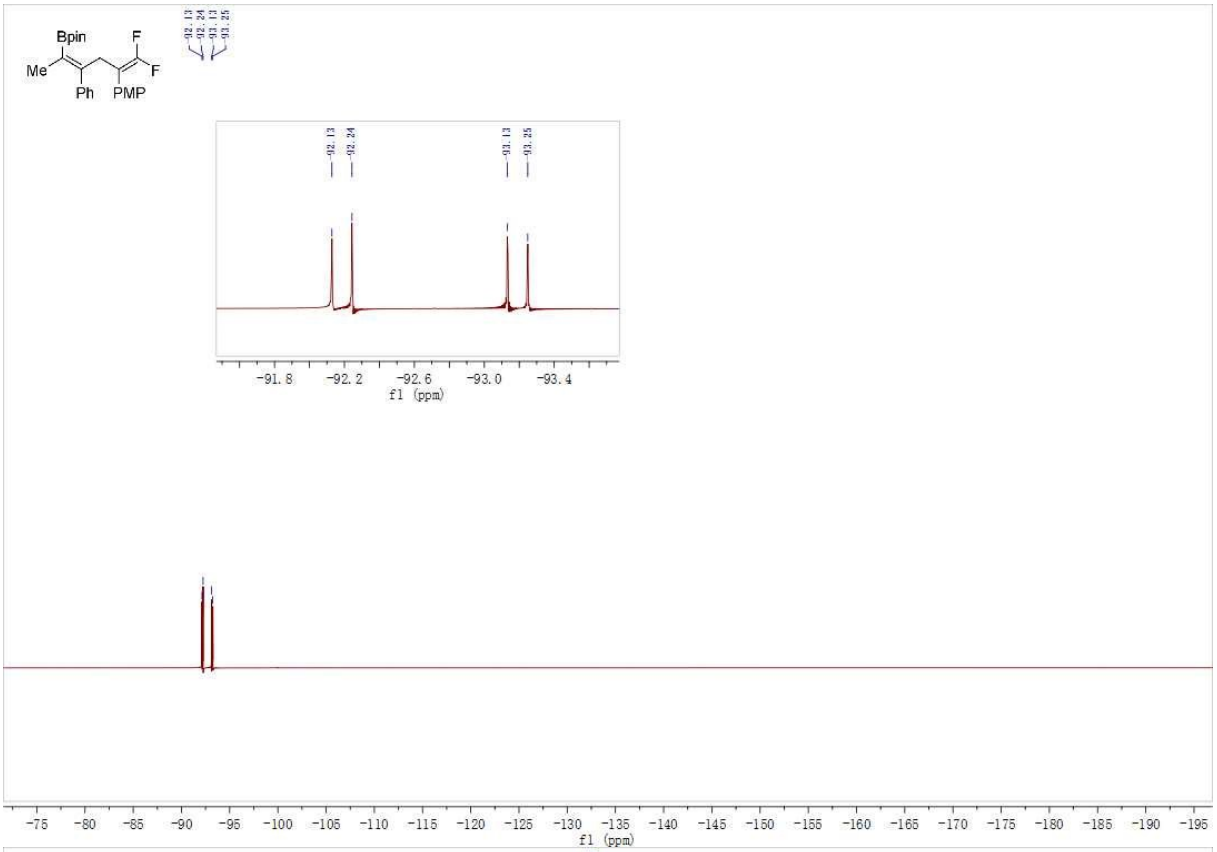
(Z)-2-(6,6-difluoro-5-(4-methoxyphenyl)-3-phenylhexa-2,5-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)

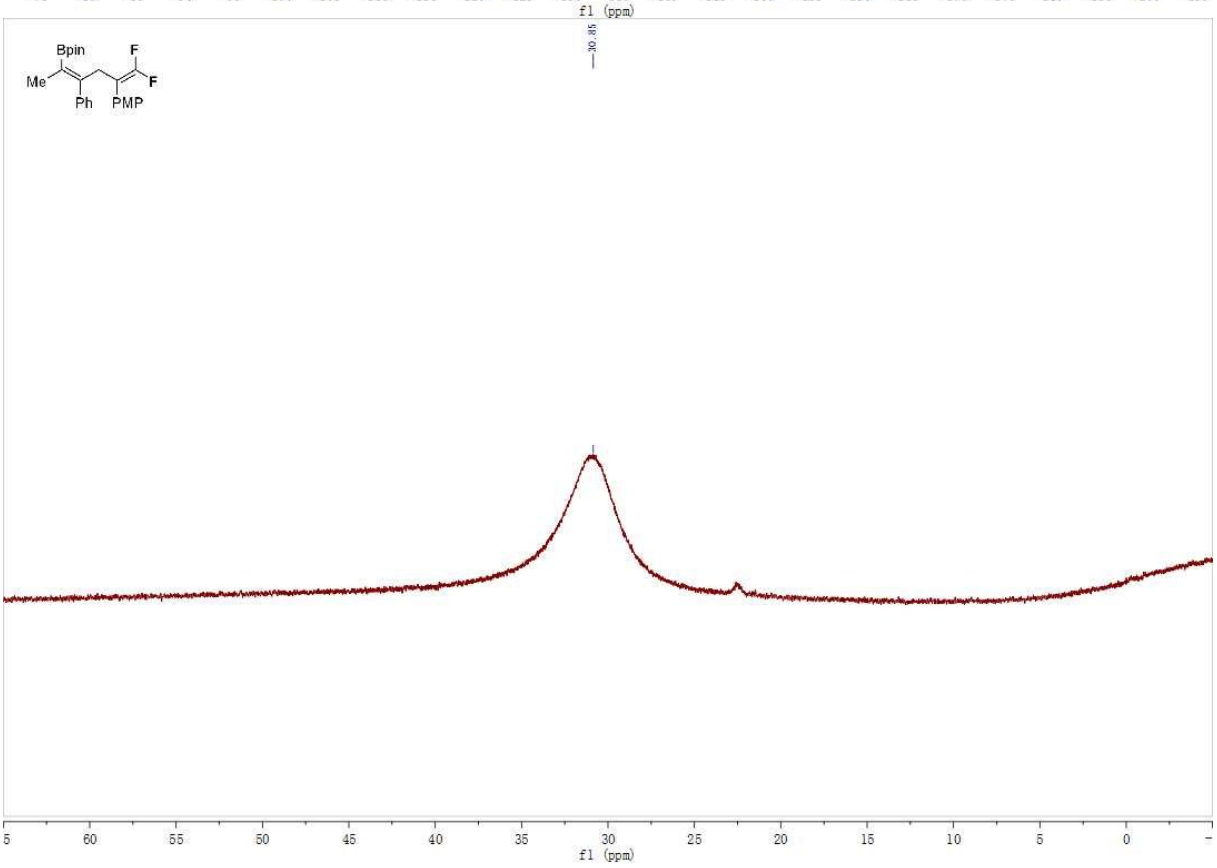


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (49.6 mg, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.17 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.86 (dd, *J* = 6.9, 5.6 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 2H), 3.79 (s, 3H), 1.48 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.38, 156.65, 152.70 (dd, *J* = 219.2, 69.9 Hz), 141.80, 129.94, 127.95, 127.68, 126.45, 125.80, 113.74, 113.31, 90.43 (dd, *J* = 20.8, 13.3 Hz), 83.22, 55.19, 34.53, 24.93, 18.61. ^{19}F NMR (376 MHz, $CDCl_3$) δ -92.27 (d, *J* = 43.3 Hz), -93.23 (d, *J* = 43.3 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.85. HRMS (ESI^+): Calcd for $C_{25}H_{29}BF_2O_3$ $[H]^+$: 427.2256, Found: 427.2265.

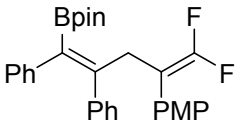

Bpin
F
Me
F
Ph
PMP
f1 (ppm)


Bpin
F
Me
F
Ph
PMP
f1 (ppm)

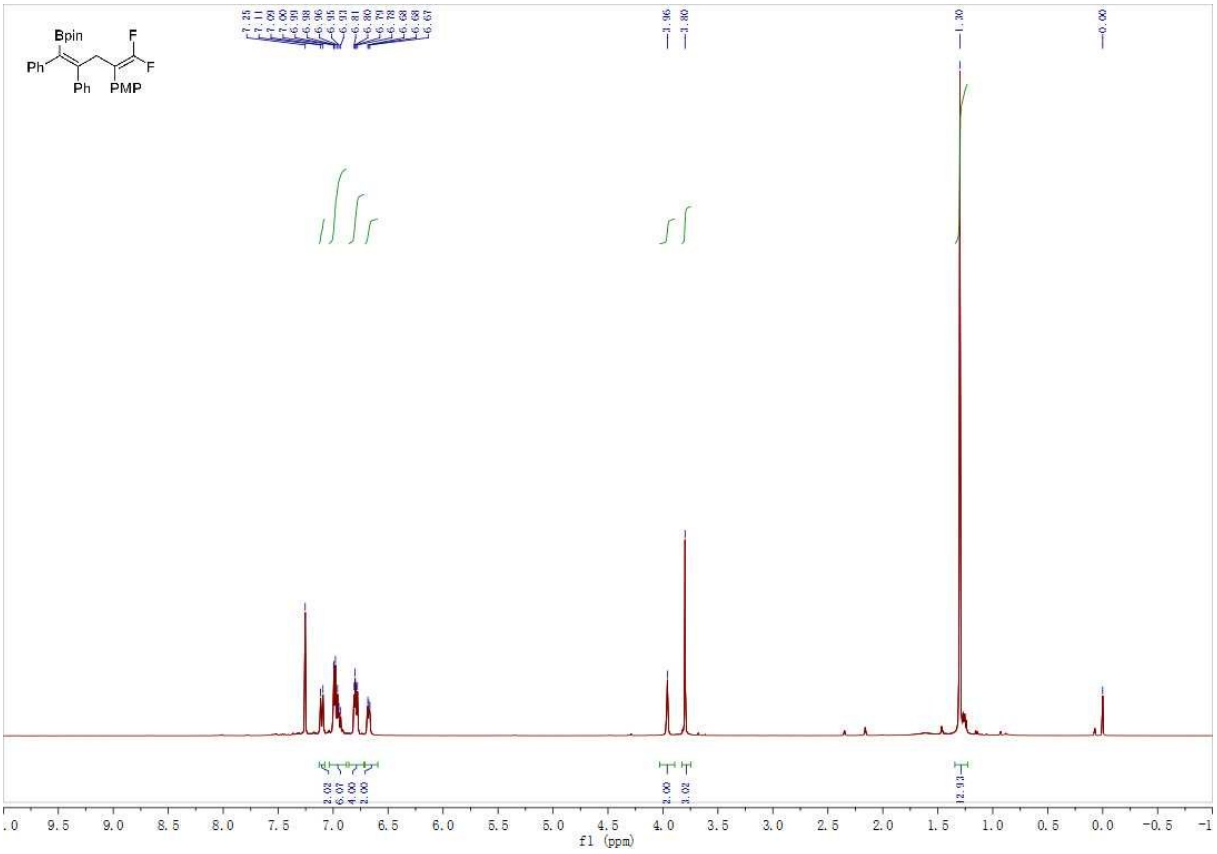


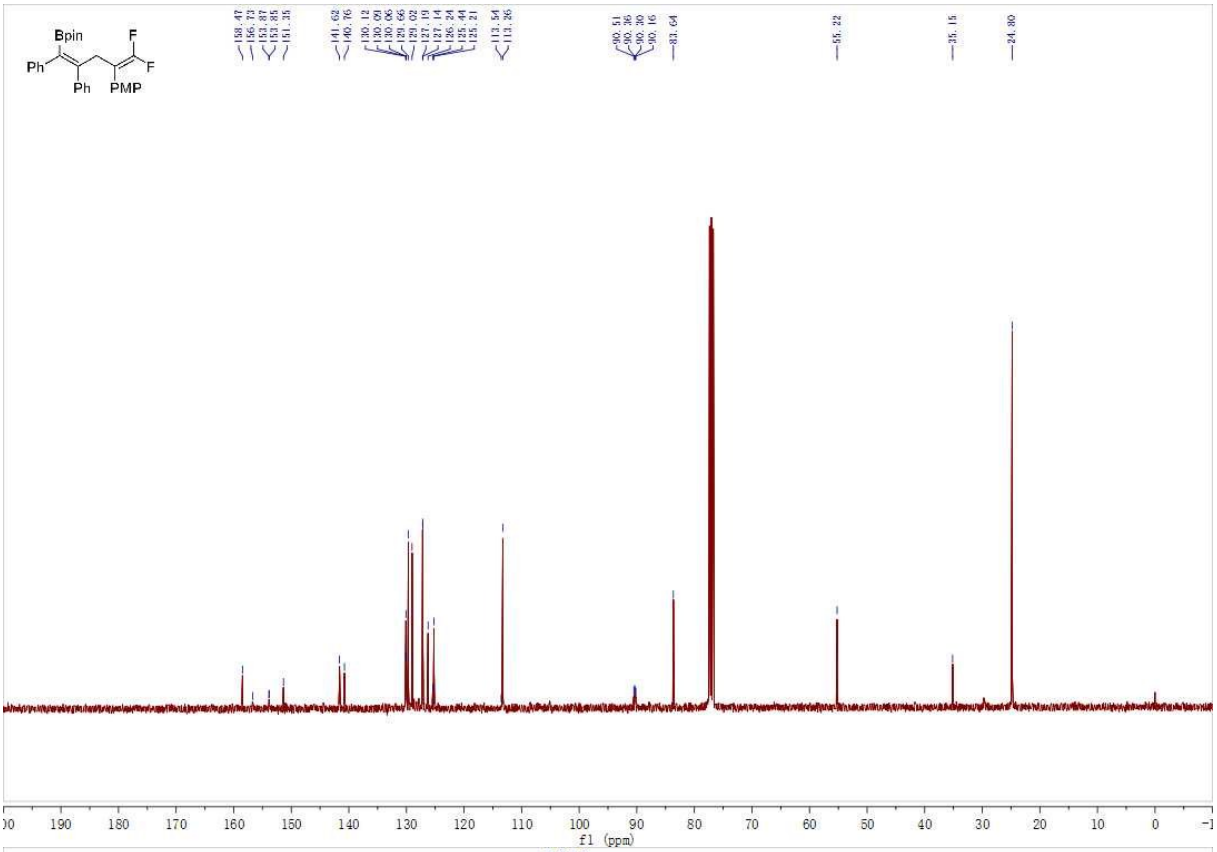


(Z)-2-(5,5-difluoro-4-(4-methoxyphenyl)-1,2-diphenylpenta-1,4-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as white solid (61 mg, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 2H), 7.02 - 6.91 (m, 6H), 6.82 - 6.77 (m, 4H), 6.72 - 6.64 (m, 2H), 3.96 (s, 2H), 3.80 (s, 3H), 1.30 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.47, 153.86 (dd, *J* = 288.5, 287.3 Hz), 151.35, 141.62, 140.76, 130.09, 129.66, 129.02, 127.19, 127.14, 126.24, 125.44, 125.21, 113.54, 113.26, 90.33 (dd, *J* = 20.5, 14.4 Hz), 83.64, 55.22, 35.15, 24.80. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.62 (d, *J* = 42.8 Hz), -92.56 (d, *J* = 42.8 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.73. HRMS (ESI^+): Calcd for $C_{30}H_{31}BF_2O_3$ $[H]^+$: 489.2413, Found: 489.2412.




Bpin
F
Ph
F
Ph
PMP
158.47
156.73
153.87
153.85
151.35
141.62
140.76
130.12
130.08
129.66
129.02
127.19
127.14
126.24
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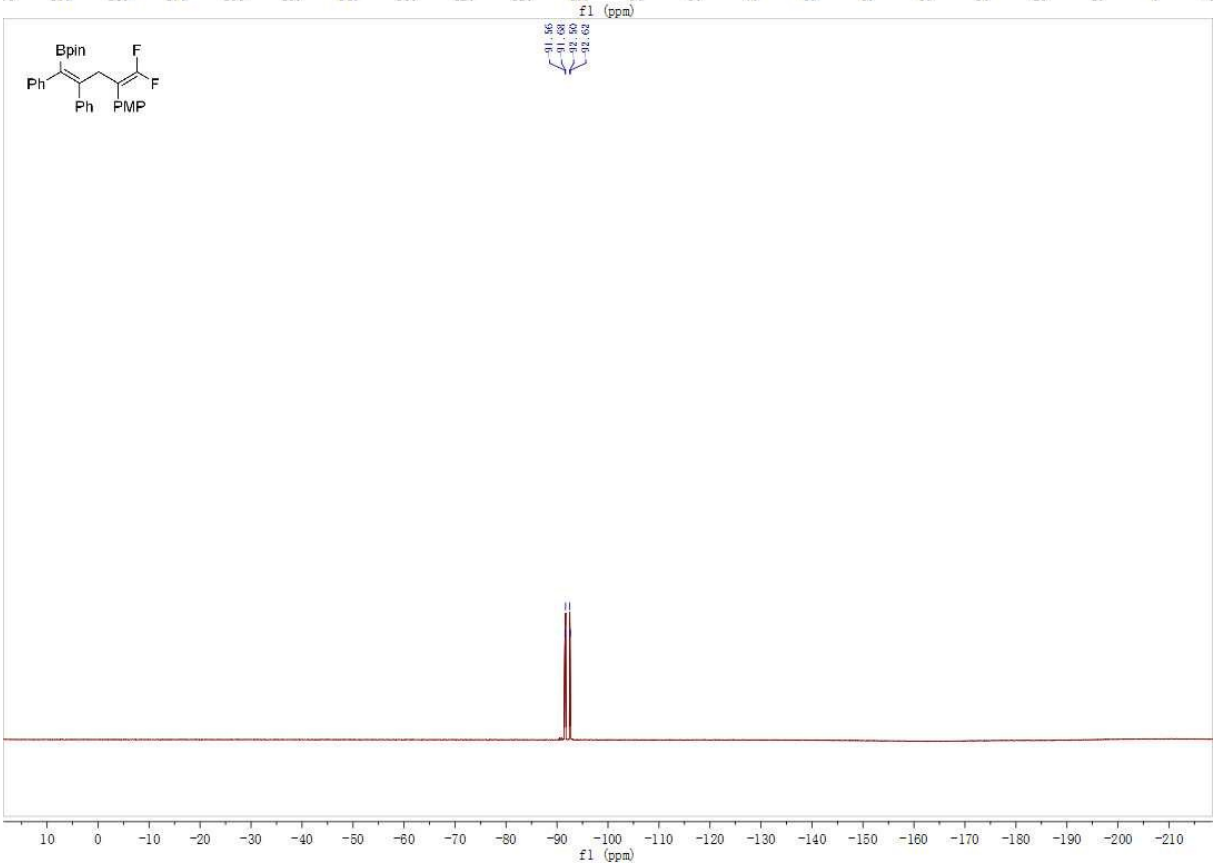
83.64
55.22
35.15
24.90
f1 (ppm)


Bpin
F
Ph
F
Ph
PMP
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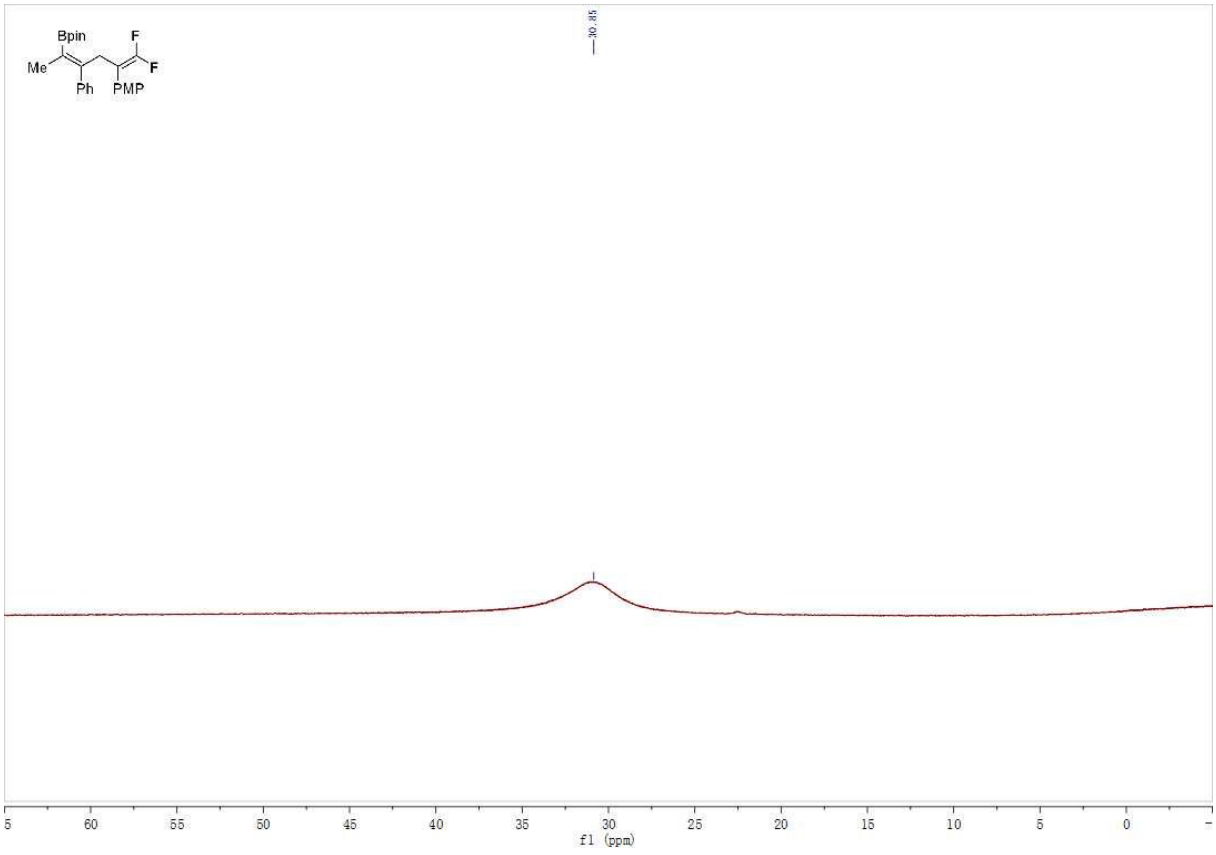
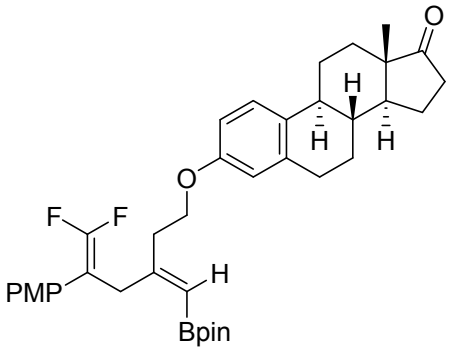
-91.68
-92.50
-92.62
f1 (ppm)

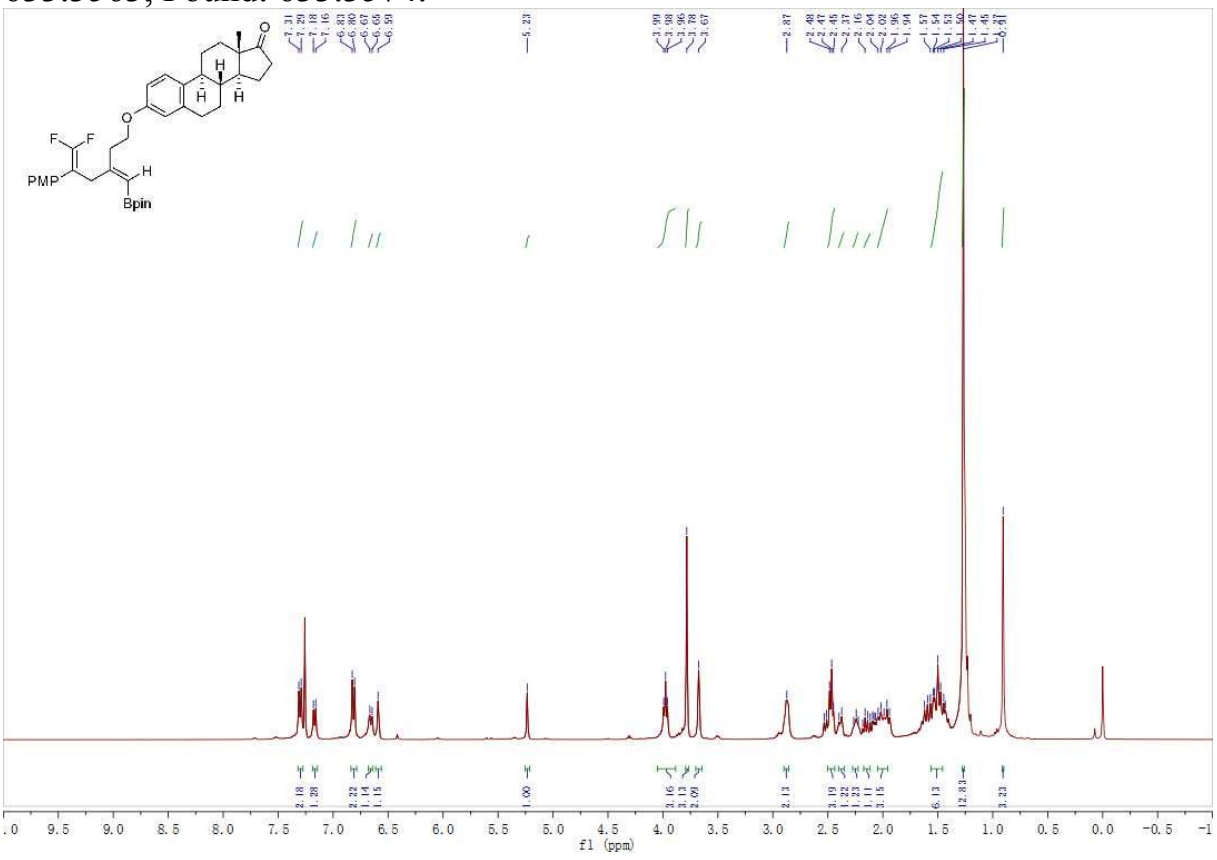


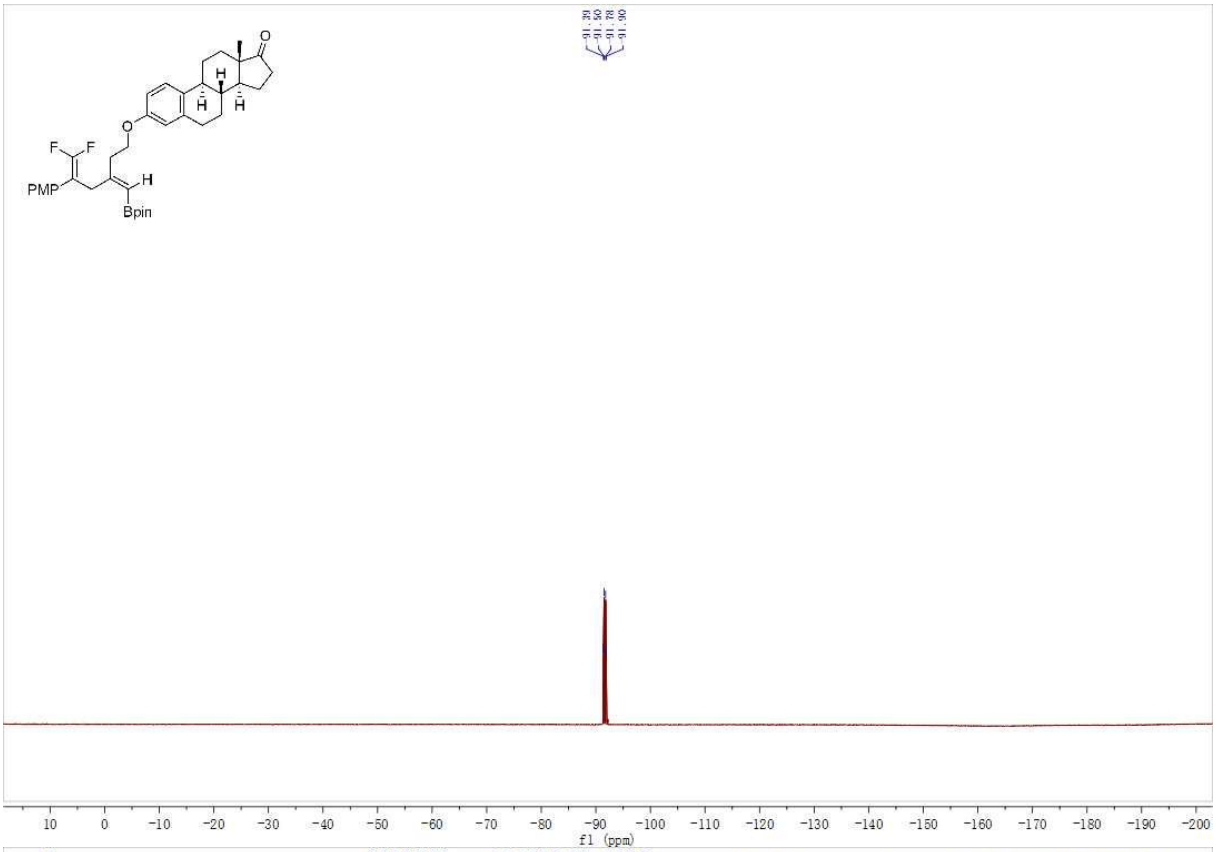
(8R,9S,13S,14S)-3-(((E)-6,6-difluoro-5-(4-methoxyphenyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)hex-5-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3q)

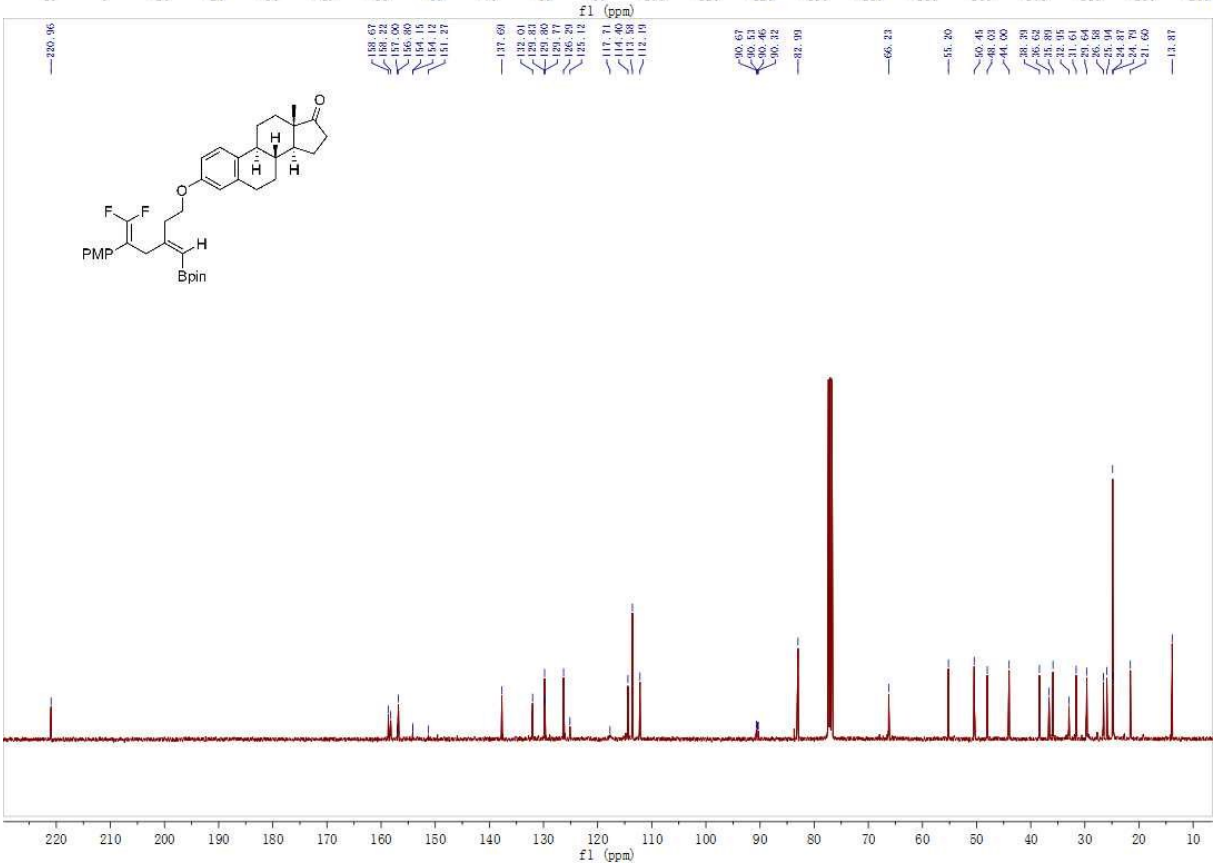


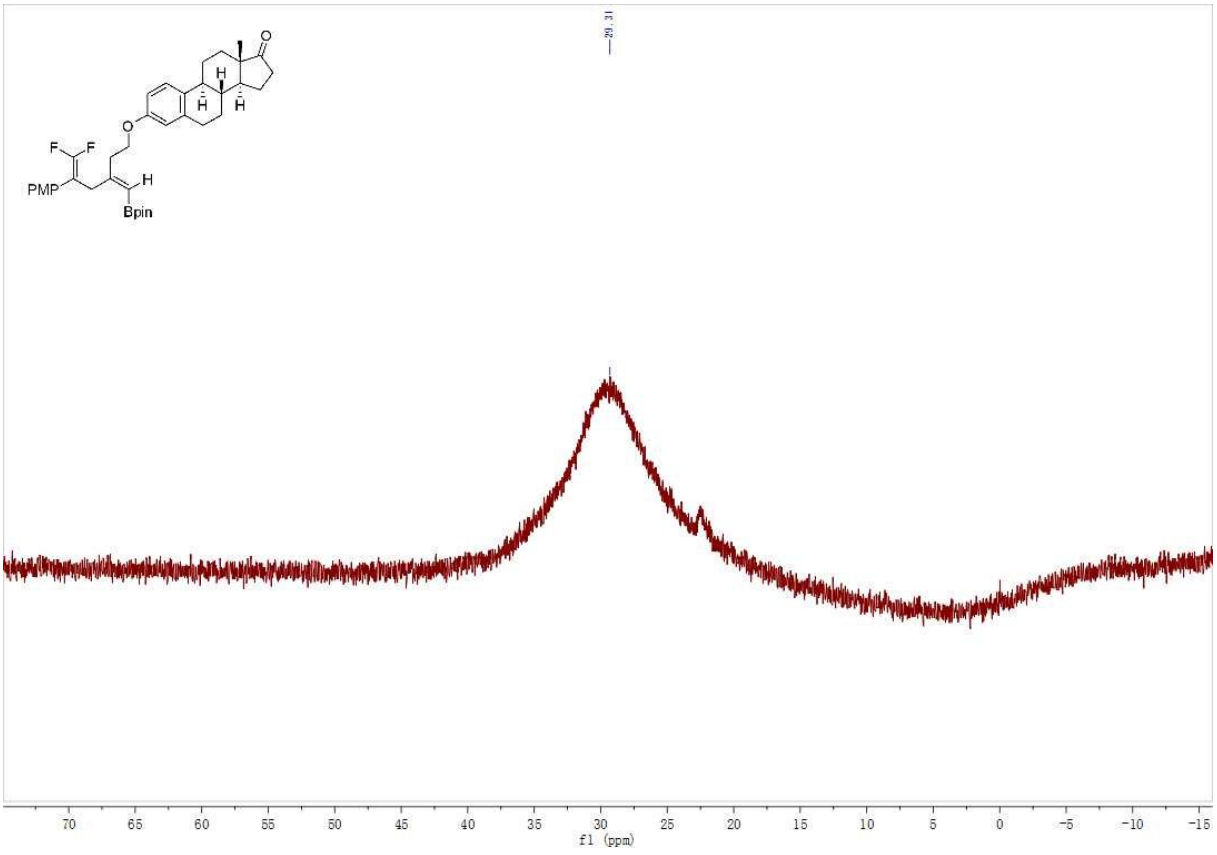
Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (10:1) as white solid (88.7 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.59 (s, 1H), 5.23 (s, 1H), 3.98 (t, *J* = 7.1 Hz, 3H), 3.78 (s, 3H), 3.67 (s, 2H), 2.97 - 2.88 (m, 2H), 2.57 – 2.43 (m, 3H). 2.47 - 2.38 (m, 1H). 2.28 - 2.20 (m,1H). 2.20 - 2.10 (m, 1H). 2.10 - 1.90 (m, 3H). 1.68 - 1.38 (m, 6H). δ 1.27 (s, 12H). 0.91 (s, 3H). ^{13}C NMR (101

MHz, $CDCl_3$) δ 220.96, 158.67, 158.22, 156.80, 154.13 (dd, *J* = 290.1, 286.8 Hz), 137.69, 132.01, 129.80, 126.29, 125.12, 117.71, 114.40, 113.58, 112.19, 90.49 (dd, *J* = 20.8, 13.8 Hz), 82.99, 66.23, 55.20, 50.45, 48.03, 44.00, 38.39, 36.62, 35.89, 32.95, 31.61, 29.64, 26.58, 25.94, 24.87, 21.60, 13.87. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.45 (d, *J* = 43.7 Hz), -91.84 (d, *J* = 43.7 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.31. HRMS (ESI^+): Calcd for $C_{38}H_{48}BF_2O_5$ $[H]^+$: 633.3563, Found: 633.3574.




F
F
PMP
H
Bpin
O
H
H
H
f1 (ppm)


F
F
PMP
H
Bpin
O
H
H
H
f1 (ppm)


29.31
O
H
H
H
O
F
F
PMP
H
Bpin
70
65
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25
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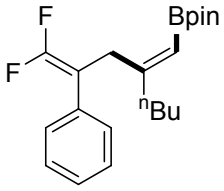
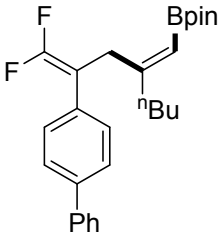
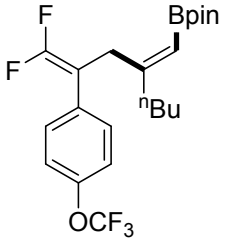
-10
-15
f1 (ppm)



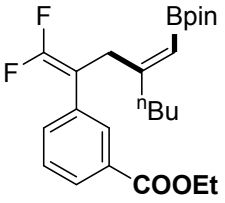
4a



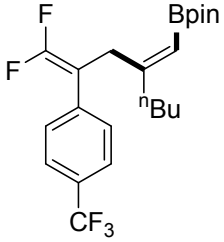
4b



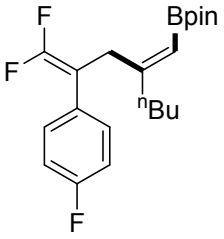
4c



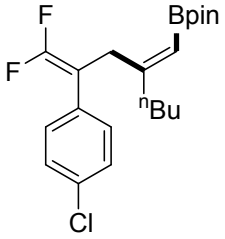
4d



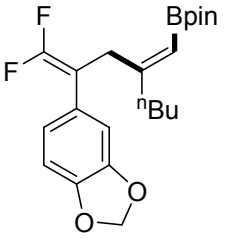
4e



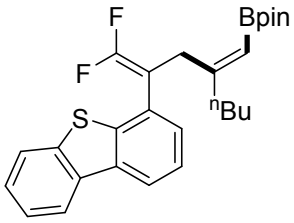
4f



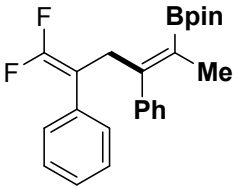
4g



4h



4i



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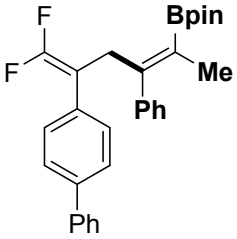
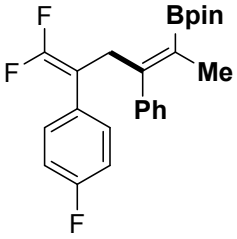
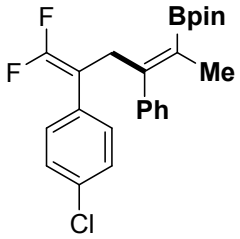


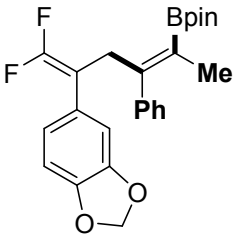
4k



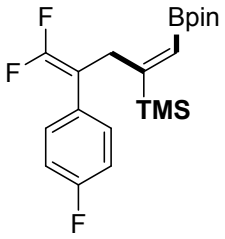
4l



4m

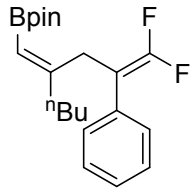


4n

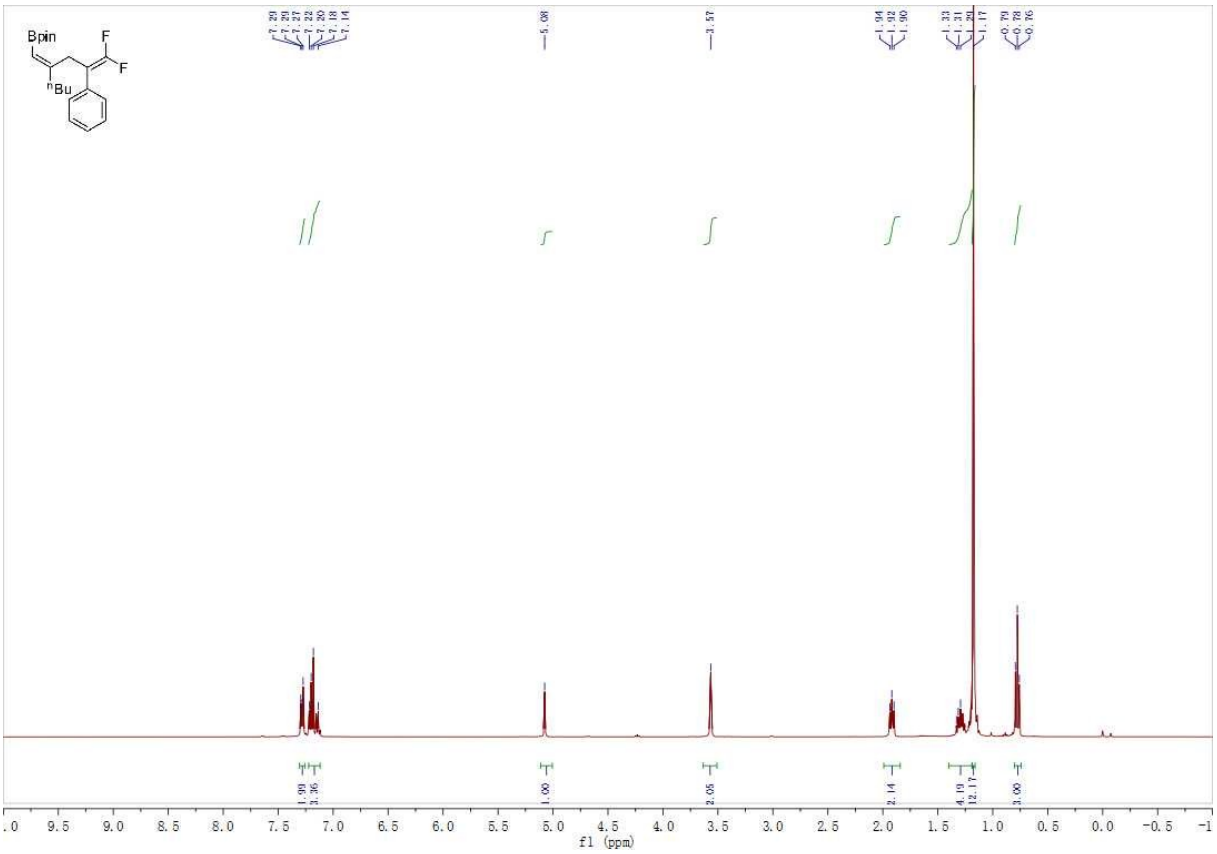


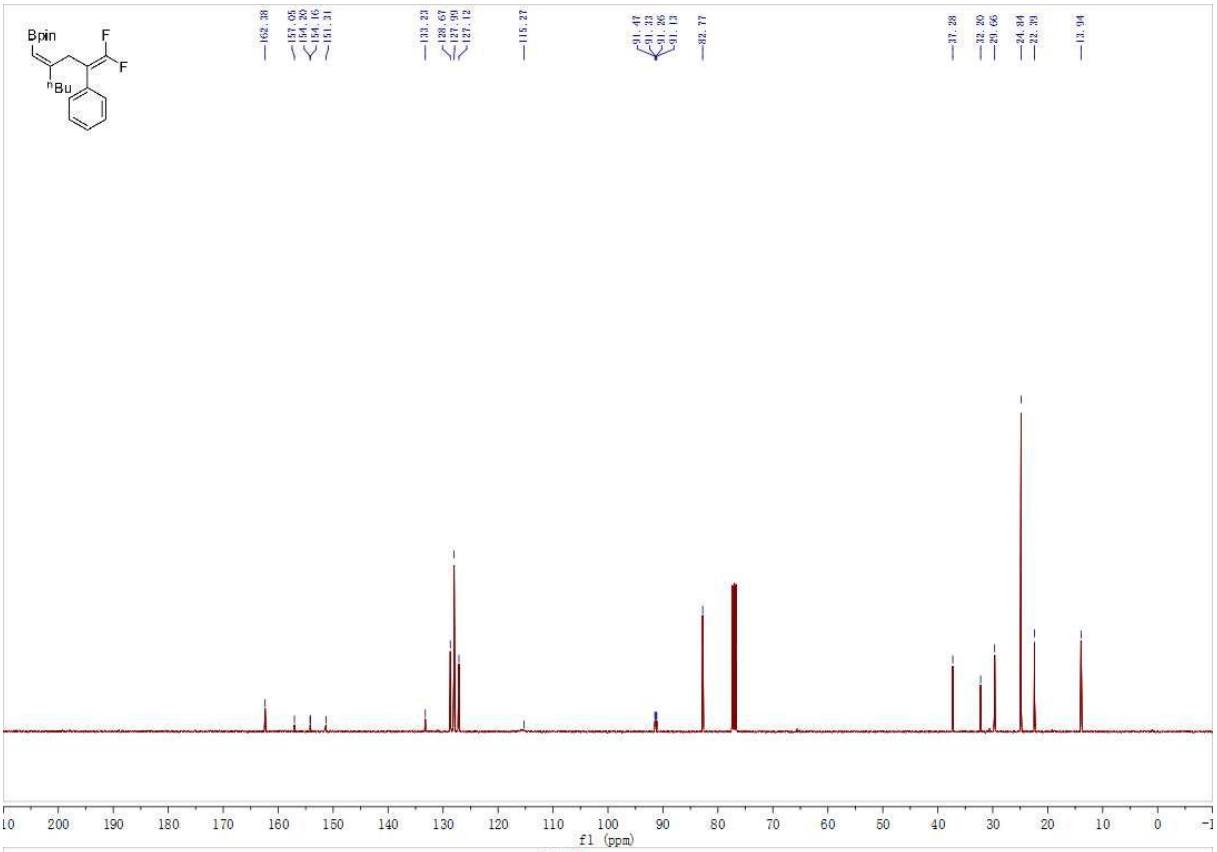
4o

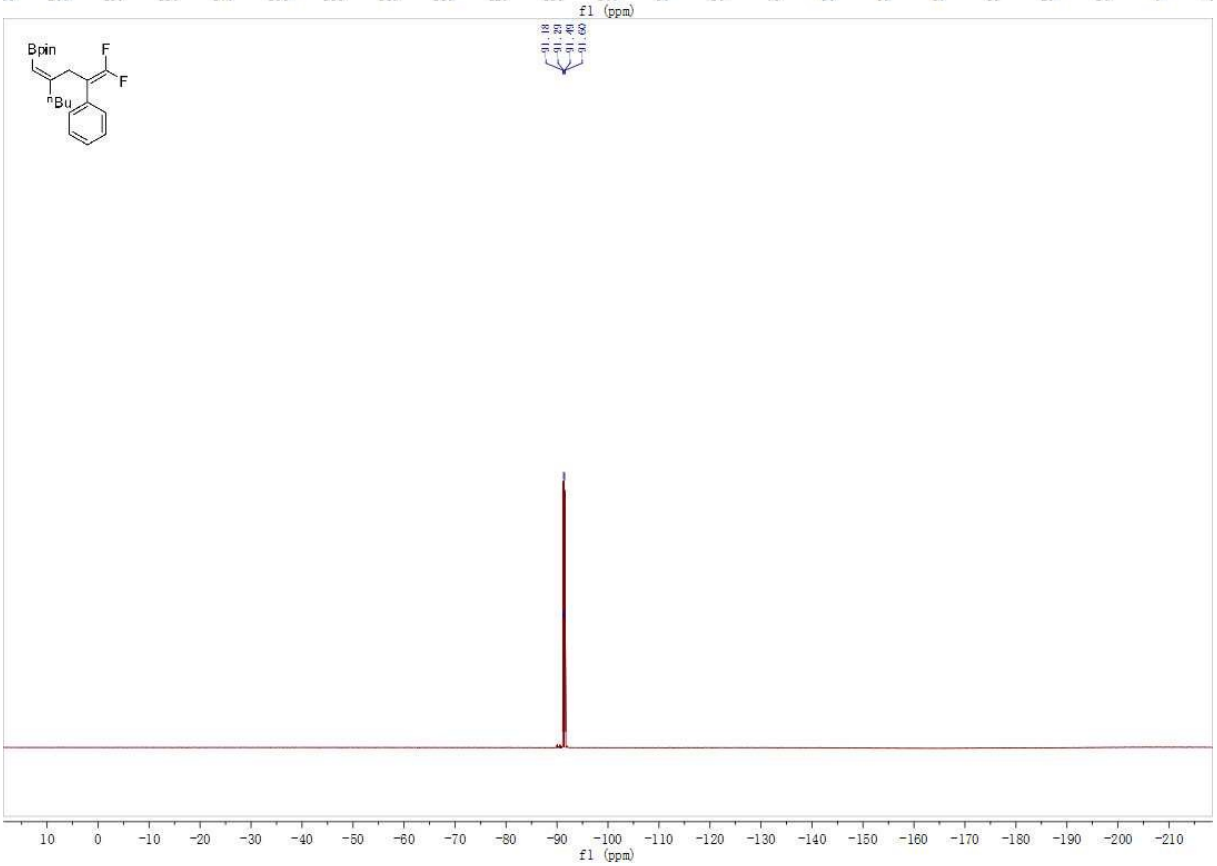
(E)-2-(3-(3,3-difluoro-2-phenylallyl)hept-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a)

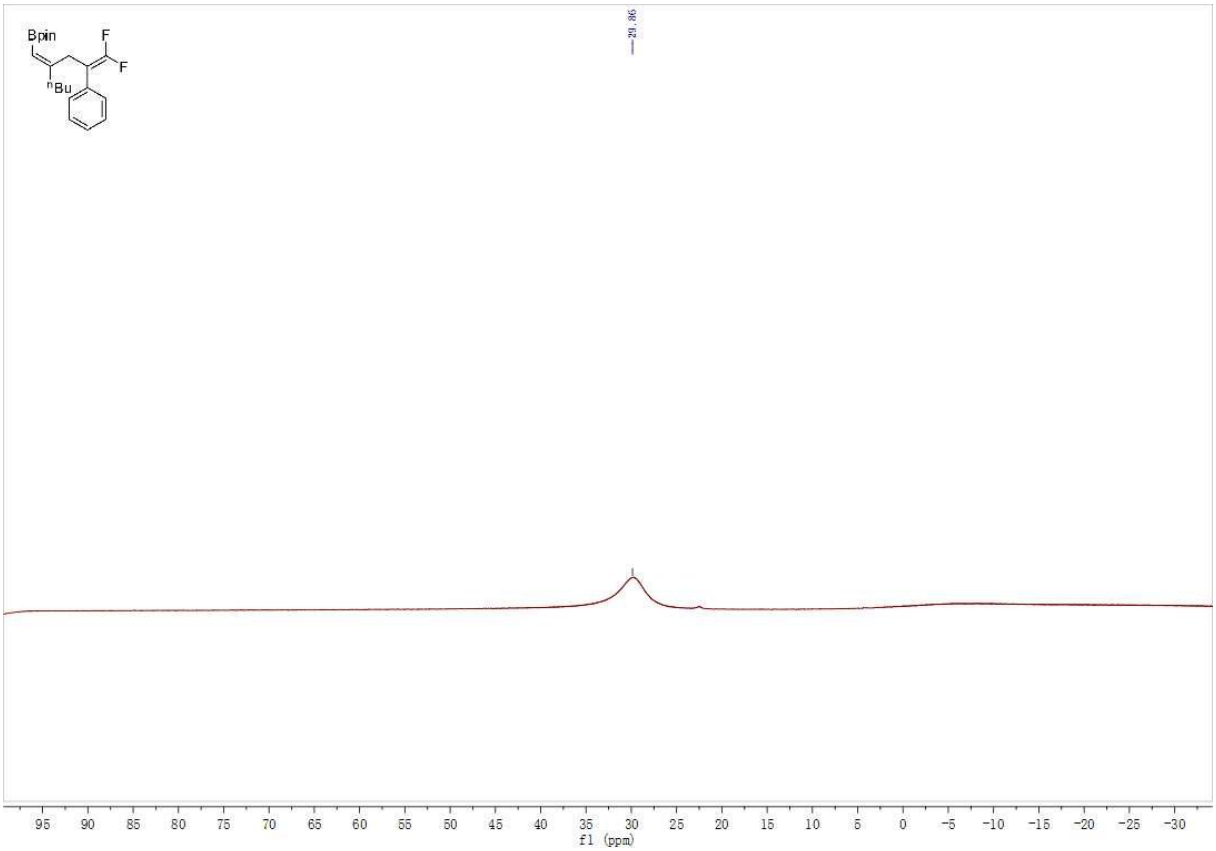


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (50 mg, 69 %).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.26 (m, 2H), 7.23 - 7.13 (m, 3H), 5.08 (s, 1H), 3.57 (s, 2H),1.92 (t, J = 7.5 Hz, 2H), 1.43 – 1.30 (m, 4H), 1.17 (s, 12H), 0.78 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.38, 154.18 (dd, J = 290.3, 286.7 Hz), 133.23, 128.67, 127.99, 127.12, 115.27, 91.30 (dd, J = 20.8, 13.4 Hz), 82.77, 37.28, 32.20, 29.66, 24.84, 22.39, 13.94. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.23 (d, J = 42.2 Hz), -91.55 (d, J = 42.2 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.86. HRMS (ESI^{+}): Calcd for $C_{21}H_{29}BF_2O_2$ [H]$^{+}$: 363.2307, Found: 363.2307.

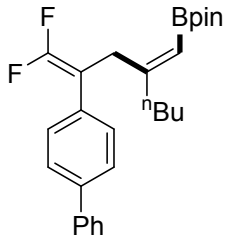



Bpin
F
F
nBu
162.38
157.65
154.30
154.16
151.31
133.23
128.67
127.90
127.12
115.27
91.47
91.33
91.26
91.13
82.77
37.28
32.20
29.66
24.04
22.39
13.94
f1 (ppm)

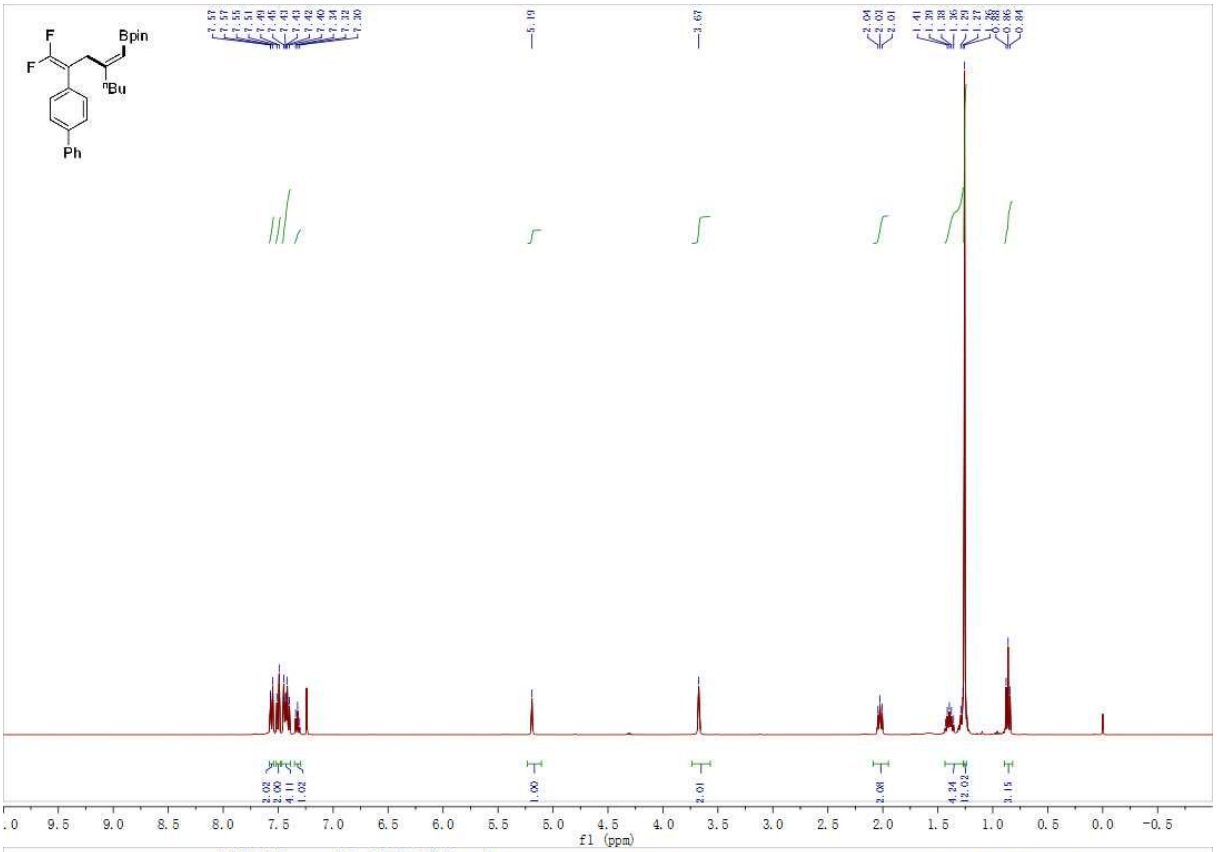

Bpin
F
F
nBu
91.18
91.29
91.40
91.60
f1 (ppm)

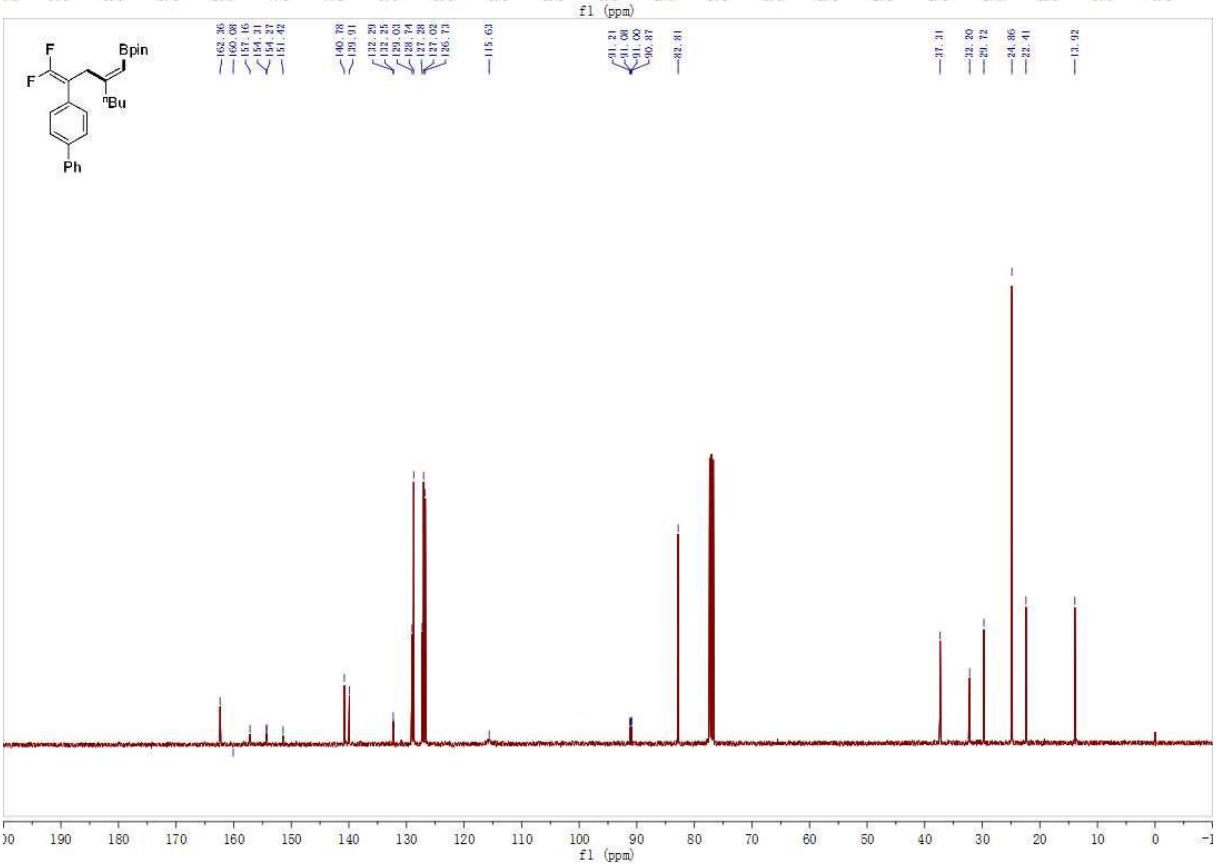


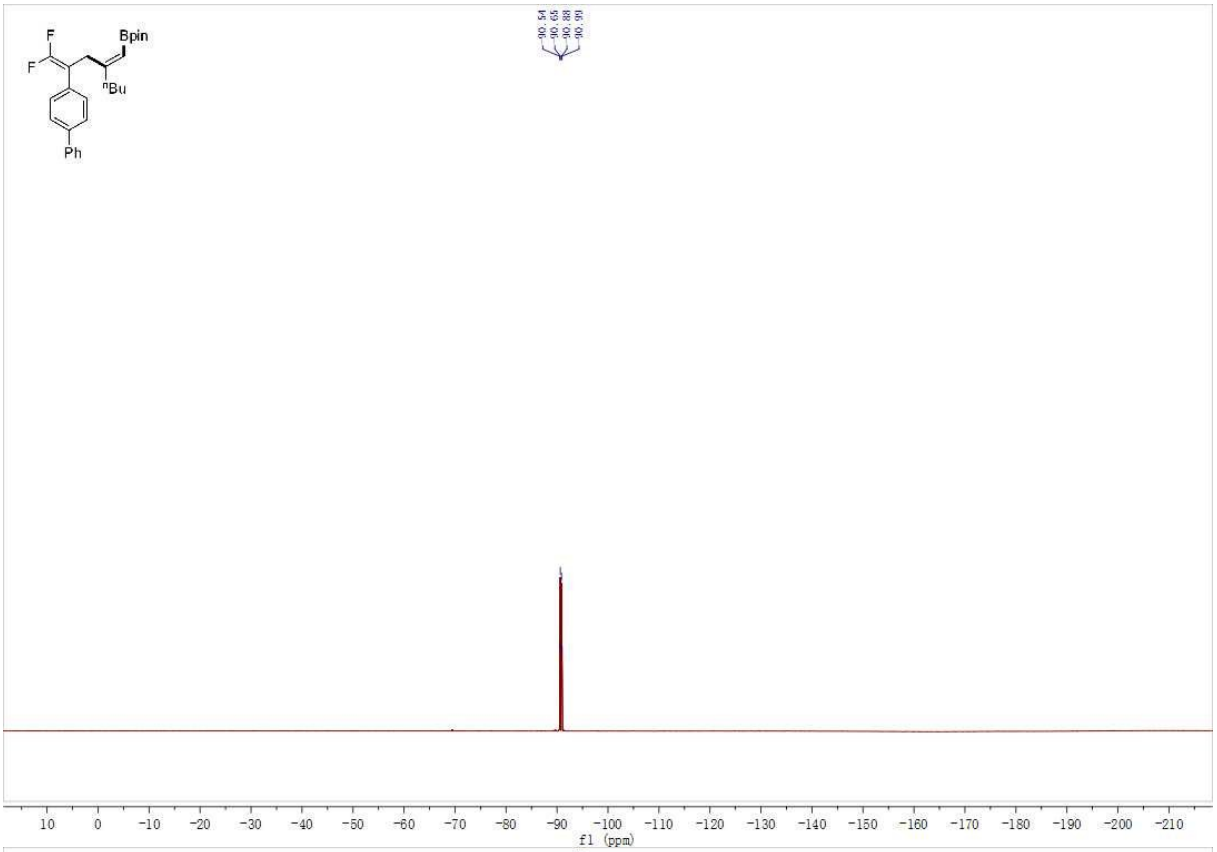
(Z)-2-(2-(2-([1,1'-biphenyl]-4-yl)-3,3-difluoroallyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4b)

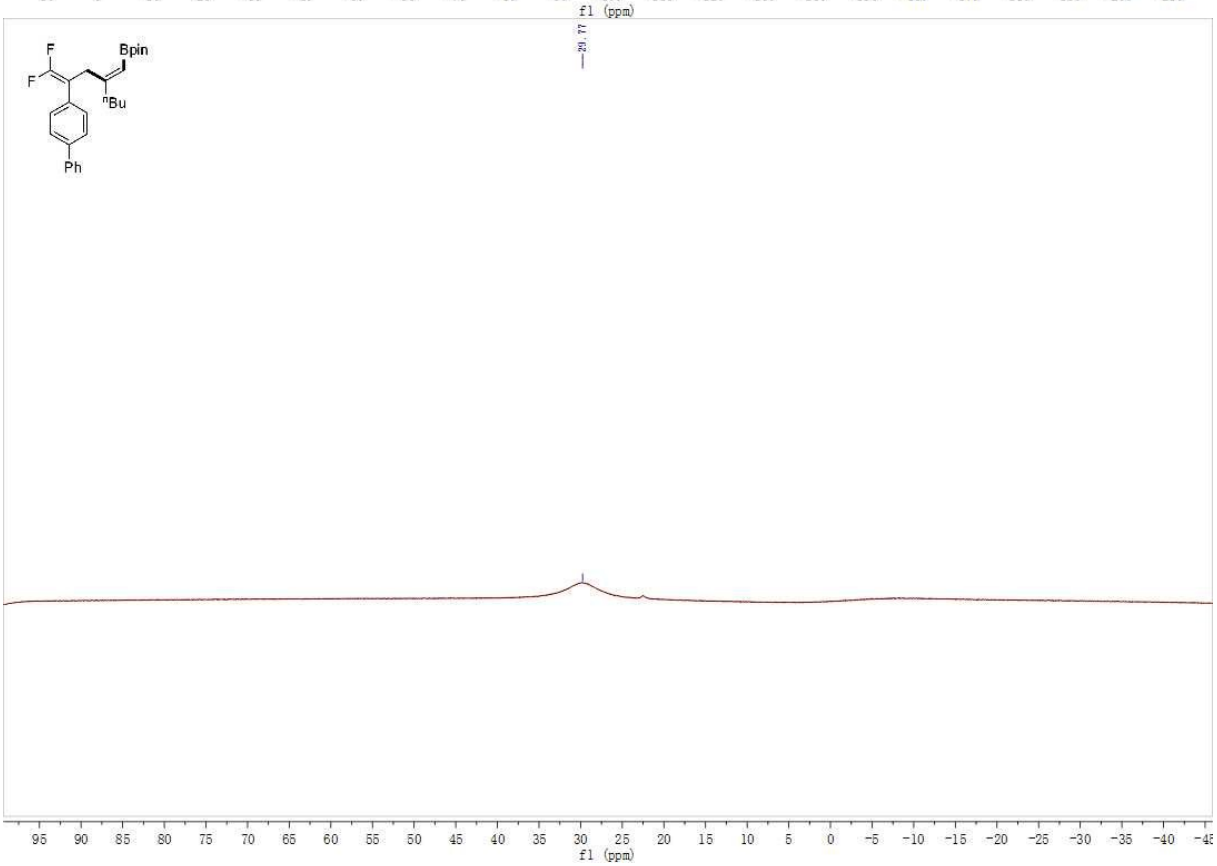


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as white solid (73.7 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.54 (m, 2H), 7.52 - 7.48 (m, 2H), 7.46 – 7.39 (m, 4H), 7.35 - 7.29 (m, 1H), 5.19 (s, 1H), 3.67 (s, 2H), 2.03(t, *J* = 7.5 Hz, 2H), 1.47 - 1.28 (m, 4H), 1.26 (s, 12H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.36, 154.29 (dd, *J* = 290.8, 287.1 Hz), 140.78, 139.91, 132.27, 129.03, 128.74, 127.28, 127.02, 126.73, 115.63, 91.04 (dd, *J* = 21.1, 13.1 Hz), 82.81, 37.31, 32.20, 29.72, 24.86, 22.41, 13.92. ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.59 (d, *J* = 41.5 Hz), -90.94 (d, *J* = 41.5 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.77. HRMS (ESI^+): Calcd for $C_{27}H_{33}BF_2O_2$ $[H]^+$: 439.2620, Found: 439.2632.

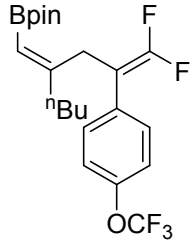

F
F
Bpin
nBu
Ph
f1 (ppm)


F
F
Bpin
nBu
Ph
f1 (ppm)

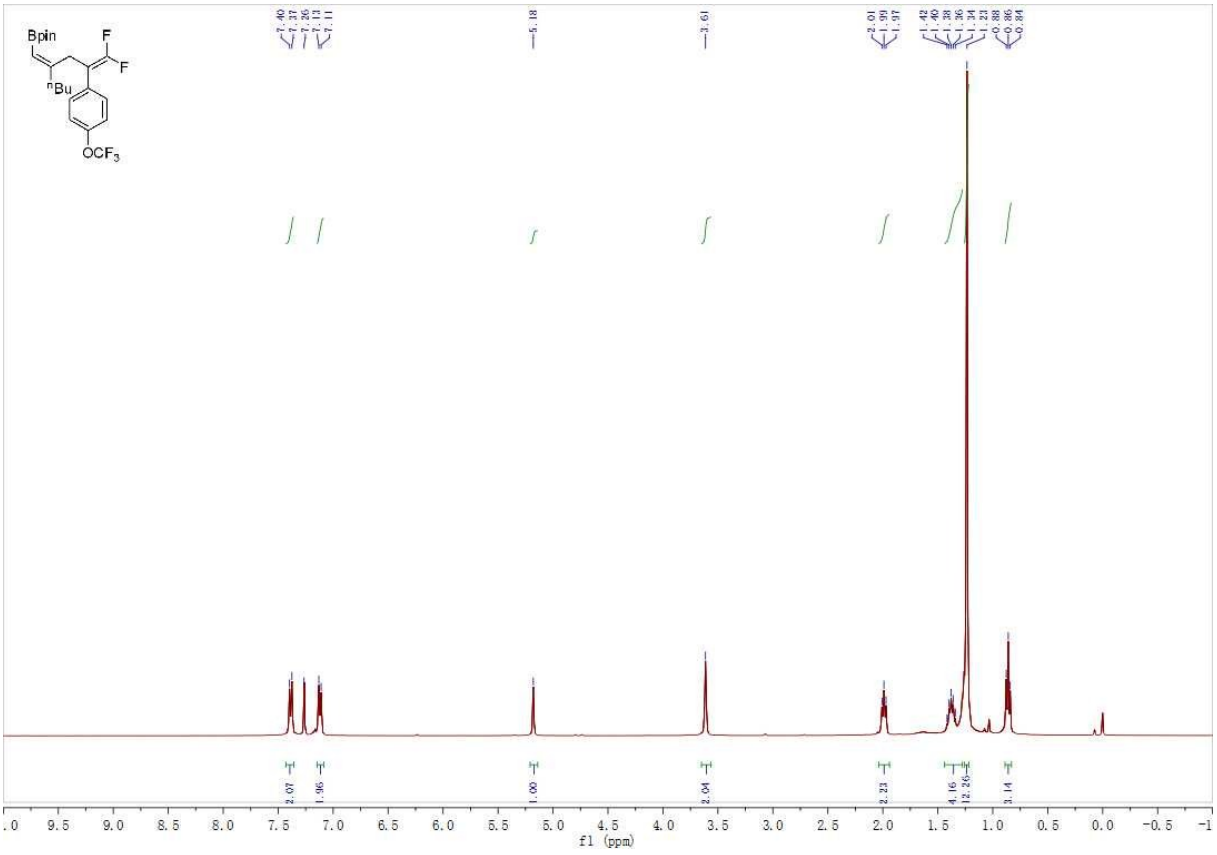

F
F
Bpin
nBu
Ph
-90.54
-90.65
-90.88
-90.99
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

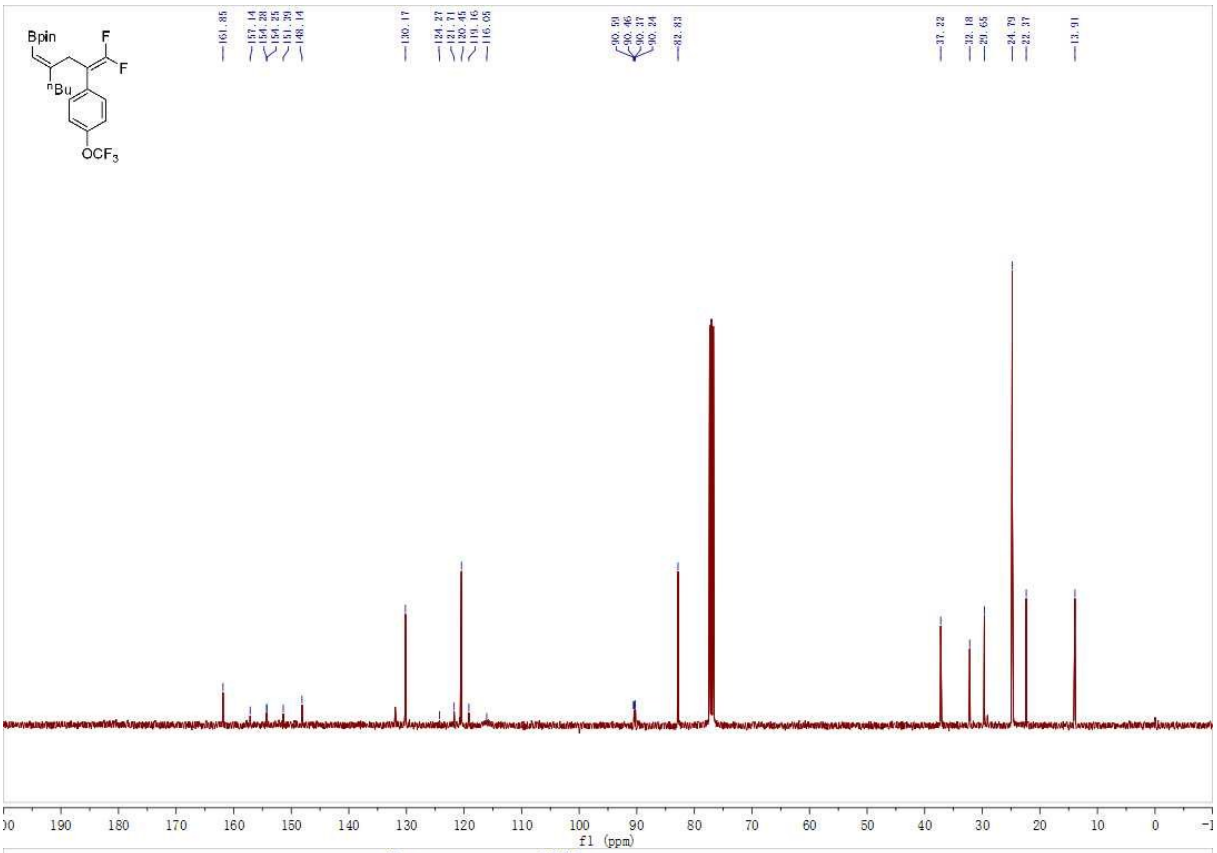

F
F
Bpin
nBu
Ph
29.77
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

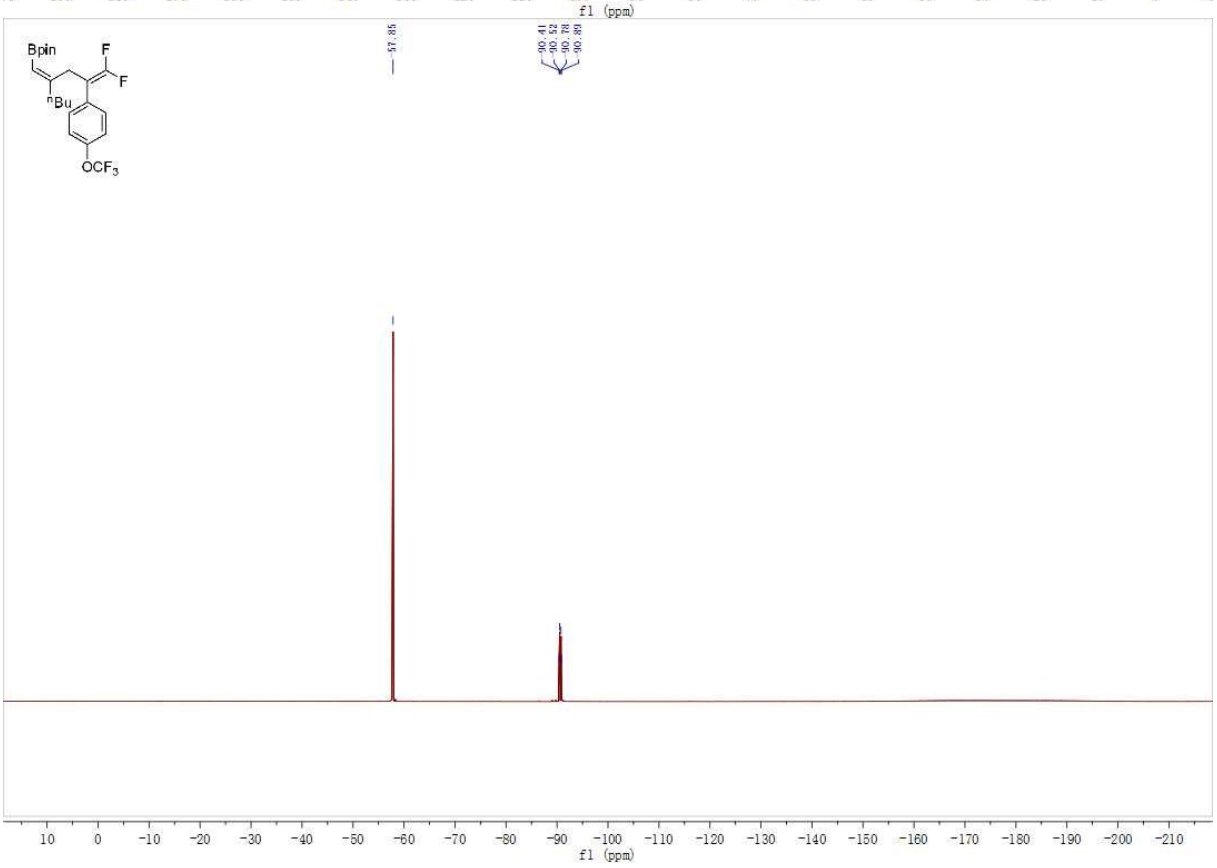
(Z)-2-(2-(3,3-difluoro-2-(4-(trifluoromethoxy)phenyl)allyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4c)

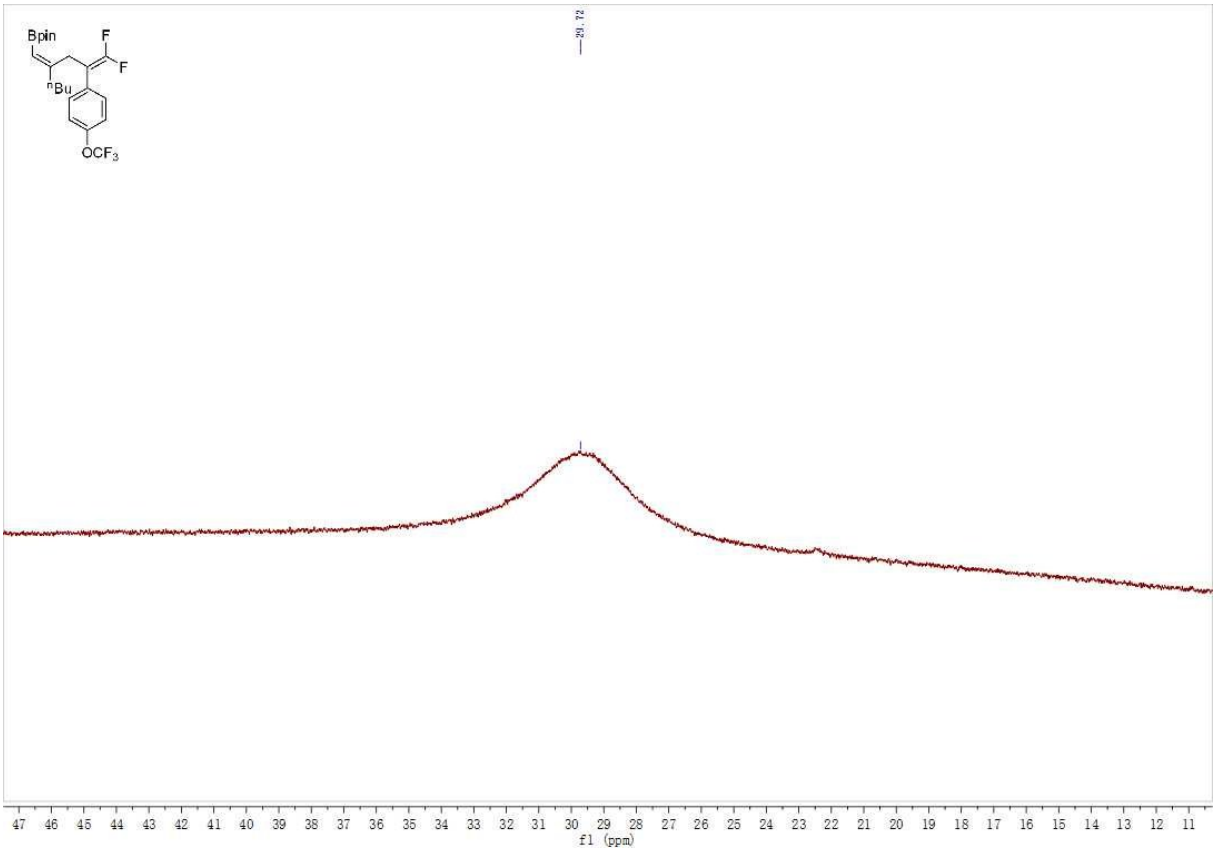


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (60 mg, 67 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz,2H), 7.12 (d, *J* = 8.3 Hz, 2H), 5.18 (s, 1H), 3.61 (s, 2H), 1.99 (t, *J* = 7.5 Hz, 2H), 1.43 - 1.33 (m, 4H), 1.23 (s, 12H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.85, 154.26 (dd, *J* = 291.0, 287.4 Hz), 148.14, 130.17, 120.45, 119.16(q, *J* = 257.5 Hz), 116.05, 90.41 (dd, *J* = 22.0, 13.4 Hz), 82.83, 37.22, 32.18, 29.65, 24.79, 22.37, 13.91. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.85, -90.47 (d, *J* = 40.8 Hz), -90.83 (d, *J* = 40.8 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.95. HRMS (ESI^+): Calcd for $C_{22}H_{28}BF_5O_3$ $[H]^+$: 447.2130, Found: 447.2115.

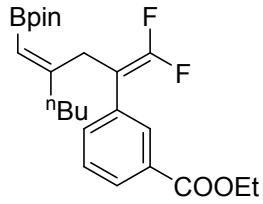



Bpin
F
F
nBu
OCF3
161.85
157.14
154.28
154.25
151.39
148.14
130.17
124.27
121.71
120.45
119.16
116.08
90.59
90.46
90.37
90.24
82.83
37.22
32.18
29.65
24.79
22.37
13.91
f1 (ppm)

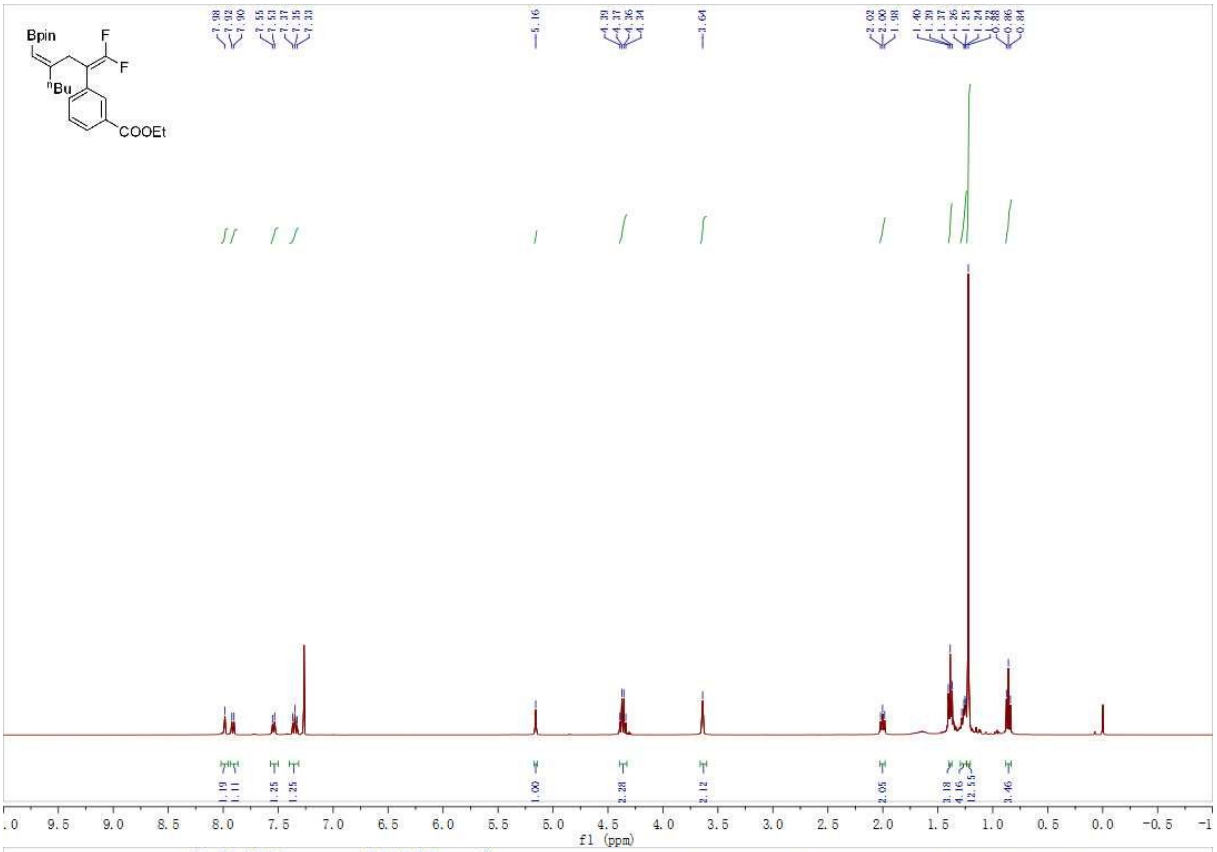

Bpin
F
F
nBu
OCF3
57.85
90.41
90.52
90.78
90.89
f1 (ppm)

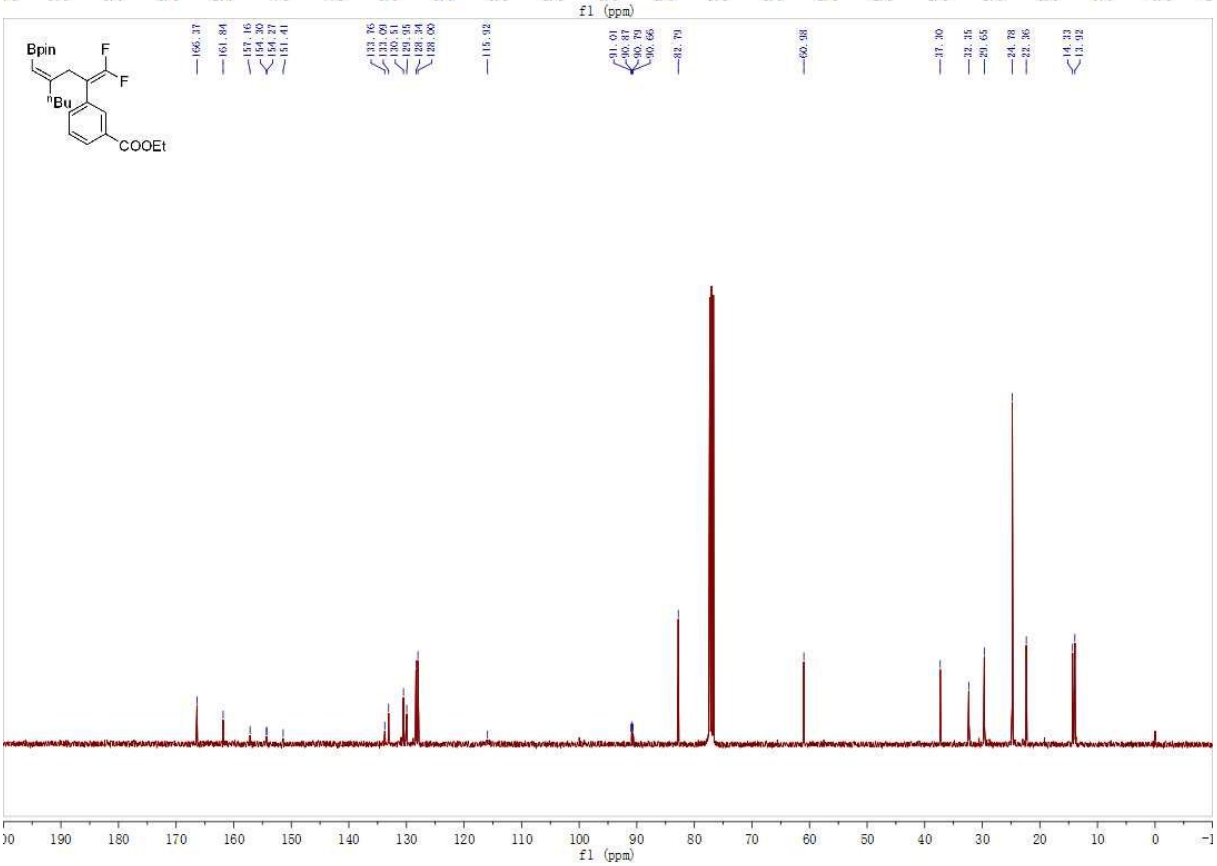


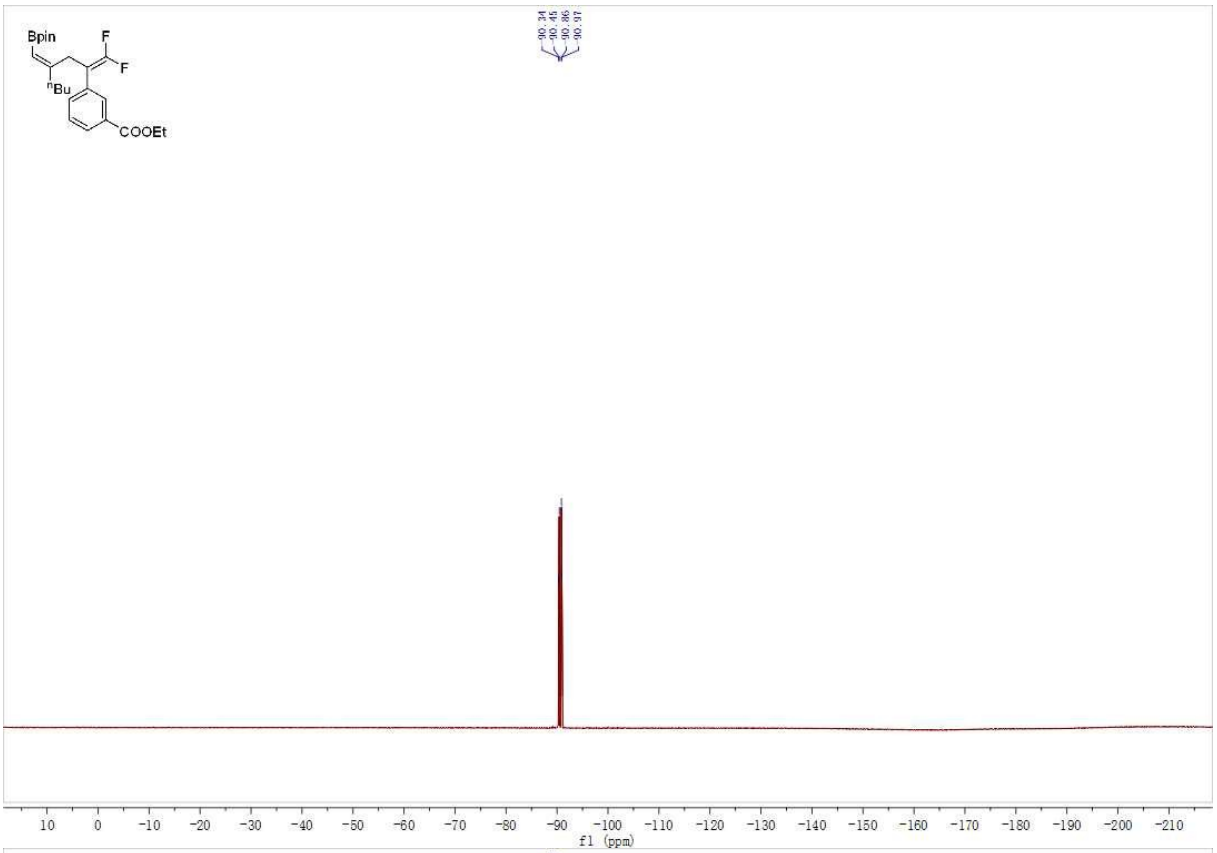
ethyl (Z)-3-(1,1-difluoro-4-((3,3,4,4-tetramethyl-1l3,2,5-bromadioxolan-1-yl)methylene)oct-1-en-2-yl)benzoate (4d)

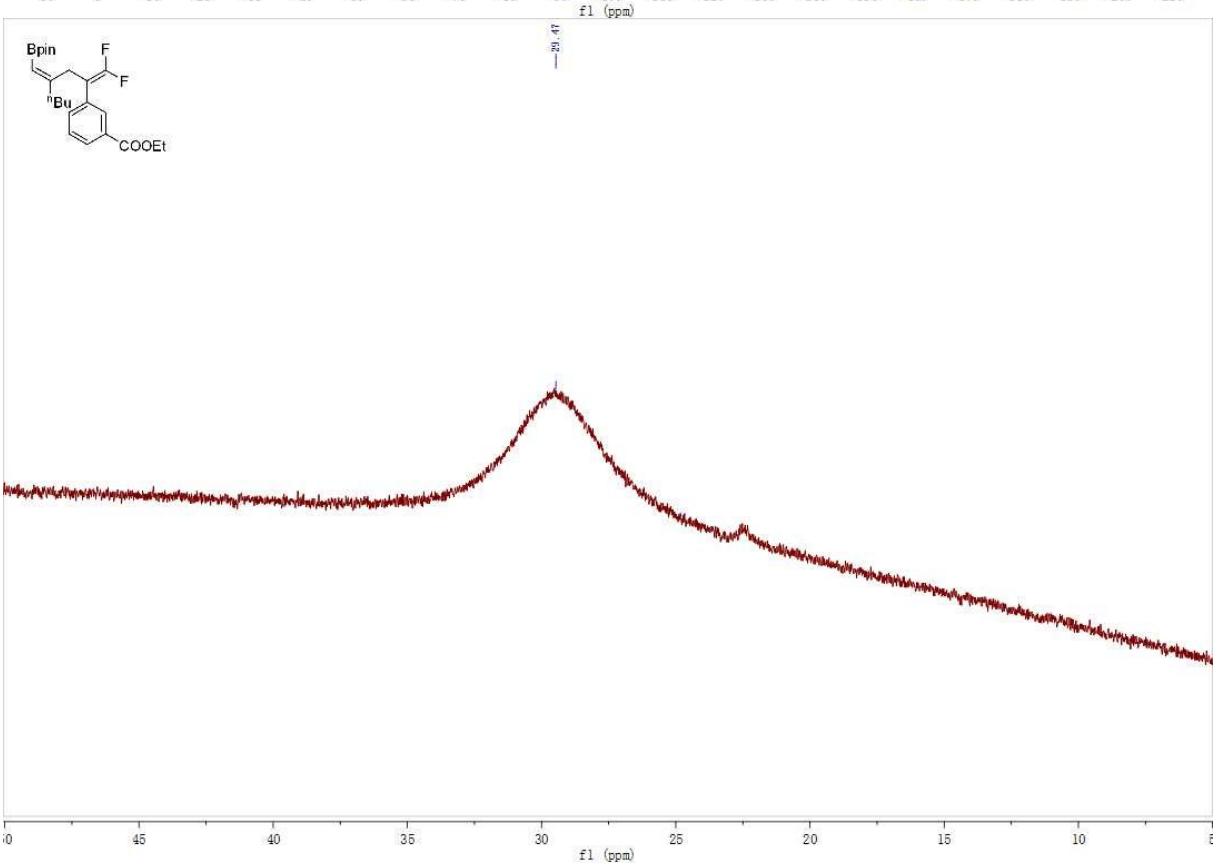


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (30:1) as thick oil (54.8 mg, 63 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 5.16 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 2.03 – 1.98 (t, *J* = 7.5 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.29 - 1.23 (m, 4H), 1.22 (s, 12H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.37, 161.84, 154.28 (dd, *J* = 290.7, 287.6 Hz), 133.76, 133.09, 130.51, 129.95, 128.34, 128.00, 115.92, 90.83 (dd, *J* = 21.9, 13.5 Hz), 82.79, 60.98, 37.30, 32.35, 29.65, 24.78, 22.36, 14.33, 13.92. ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.45 (d, *J* = 40.4 Hz), -90.92 (d, *J* = 40.4 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.47 . HRMS (ESI^+): Calcd for $C_{24}H_{33}BF_2O_4$ $[H]^+$: 435.2518, Found: 435.2519.

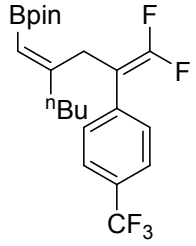

Bpin
F
F
nBu
COOEt
f1 (ppm)


Bpin
F
F
nBu
COOEt
f1 (ppm)

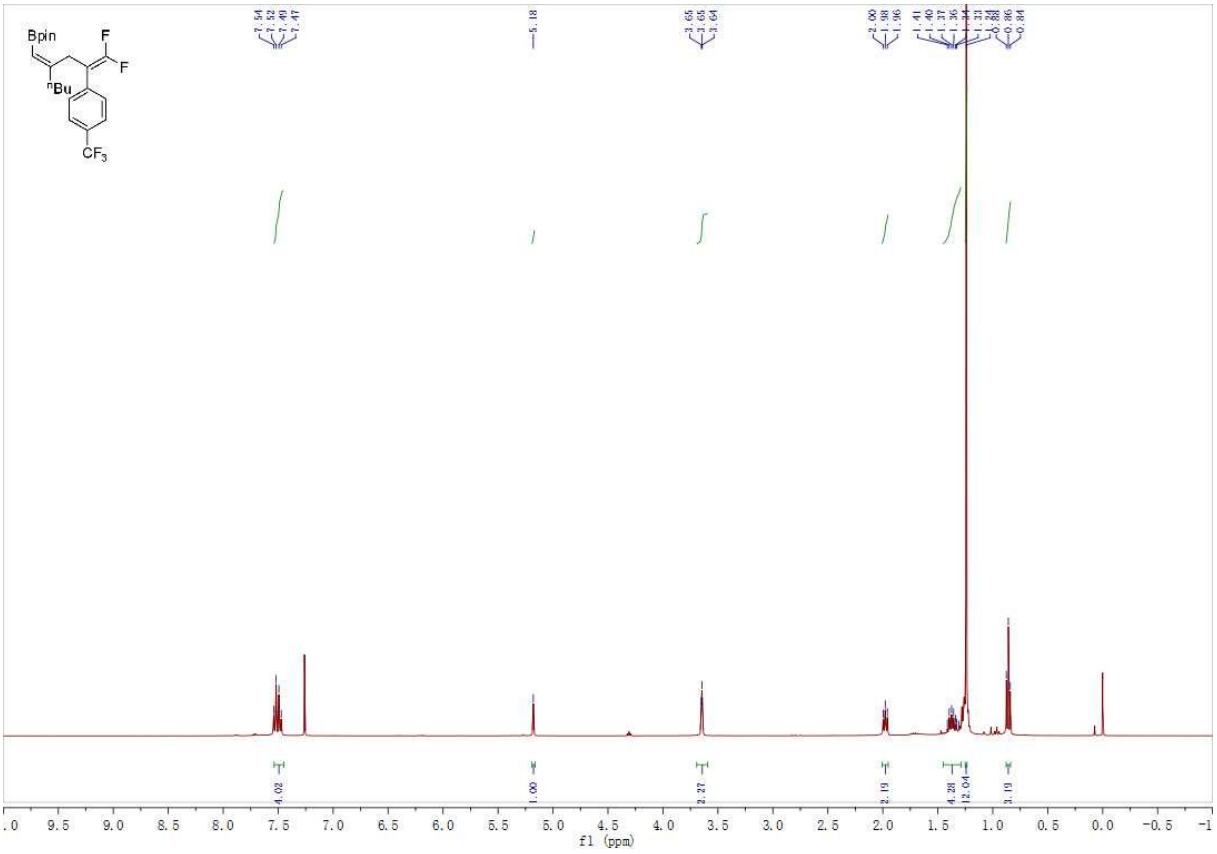

Bpin
F
F
nBu
COOEt
-90.34
-90.45
-90.86
-90.97
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

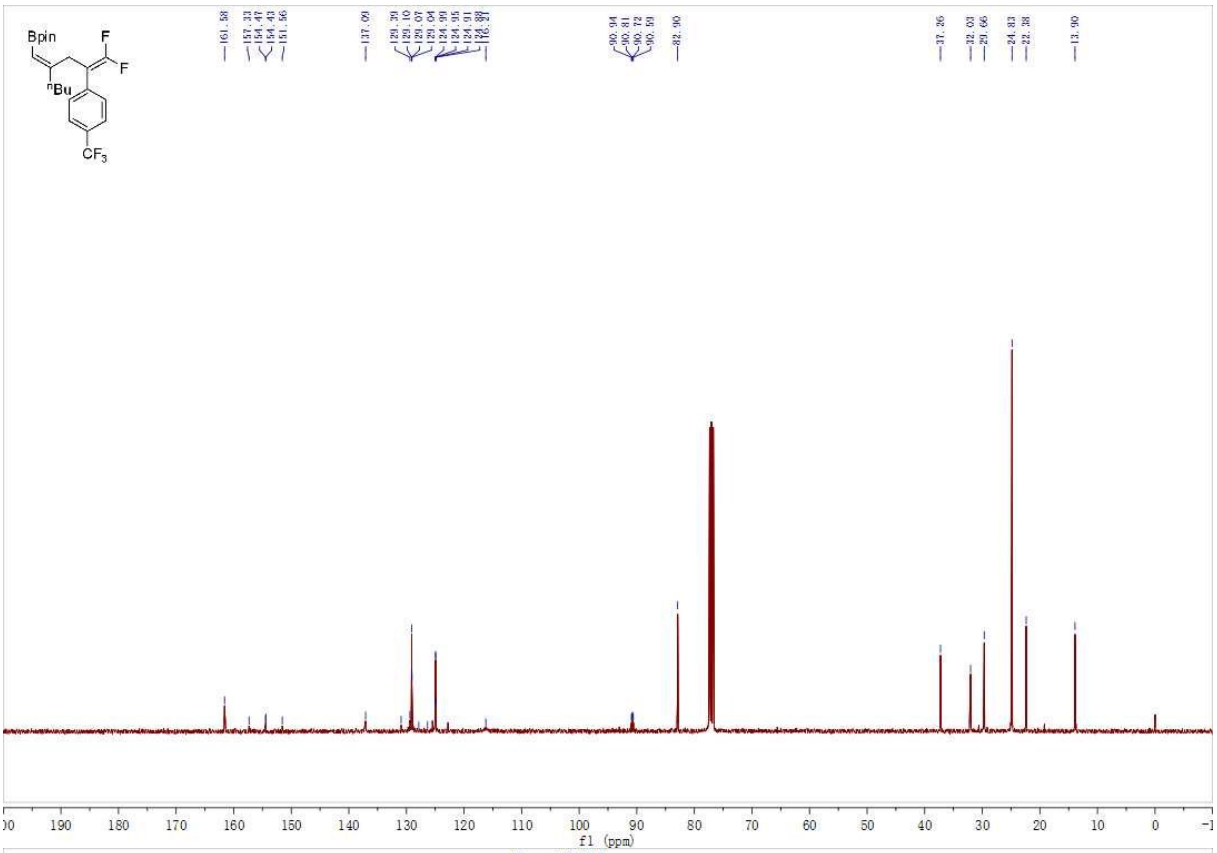

Bpin
F
F
nBu
COOEt
29.47
45 40 35 30 25 20 15 10
f1 (ppm)

(Z)-2-(2-(3,3-difluoro-2-(4-(trifluoromethyl)phenyl)allyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4e)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (51.7 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 - 7.45 (m, 4H), 5.18 (s, 1H), 3.65 (s, 2H), 2.00 – 1.95 (t, *J* = 7.6 Hz, 2H), 1.45 - 1.29 (m, 4H), 1.24 (s, 12H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.58, 154.45 (dd, *J* = 292.1, 288.3 Hz), 137.09 (s), 129.07, 128.62 (q, *J* = 155.54 Hz), 124.95, 116.21, 90.76 (dd, *J* = 21.9, 12.9 Hz), 82.90, 37.26, 32.03, 29.66, 24.83, 22.38, 13.90. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.66, -89.41 (d, *J* = 38.4 Hz), -89.71 (d, *J* = 38.4 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.12. HRMS (ESI^+): Calcd for $C_{22}H_{28}BF_5O_2$ $[H]^+$: 431.2181, Found: 431.2177.




Bpin
F
F
nBu
CF3
161.58
157.33
154.47
154.43
151.56
137.09
129.20
129.10
129.07
129.04
124.99
124.95
124.91
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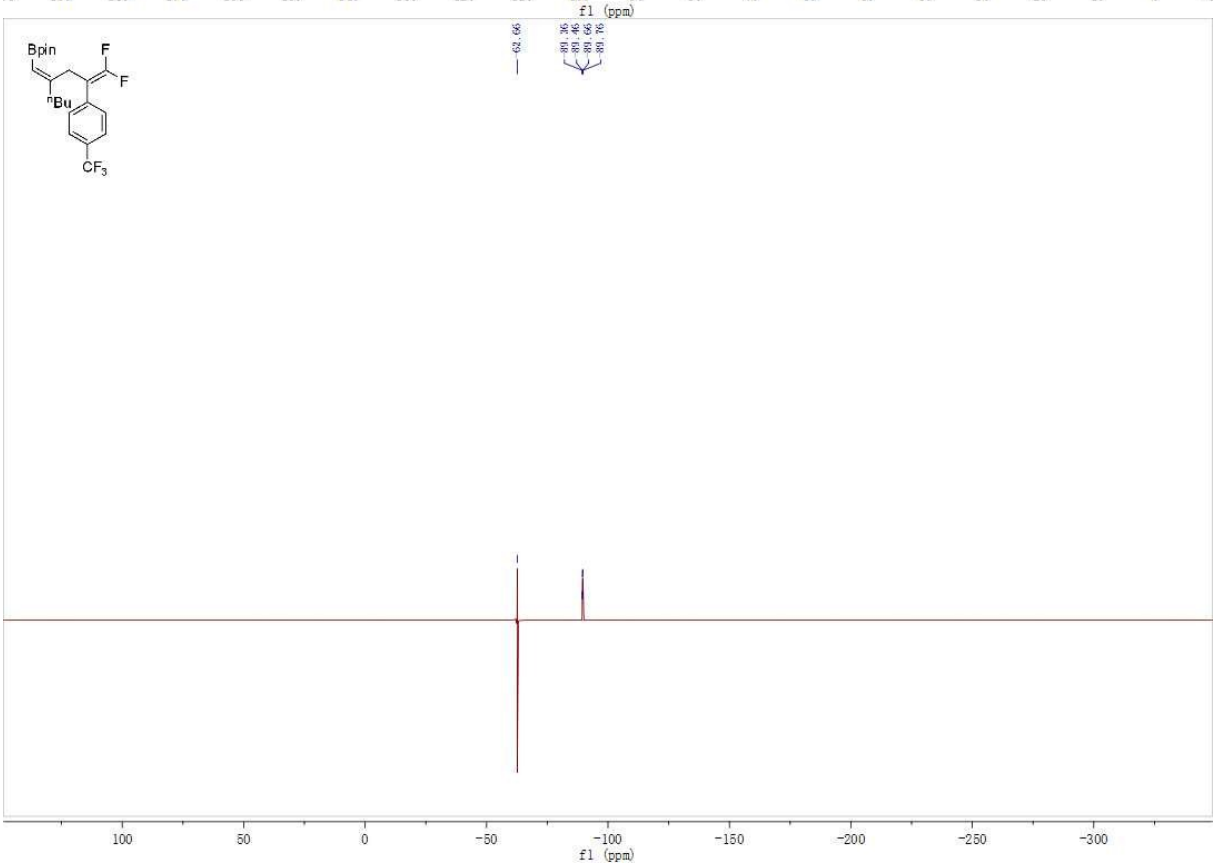
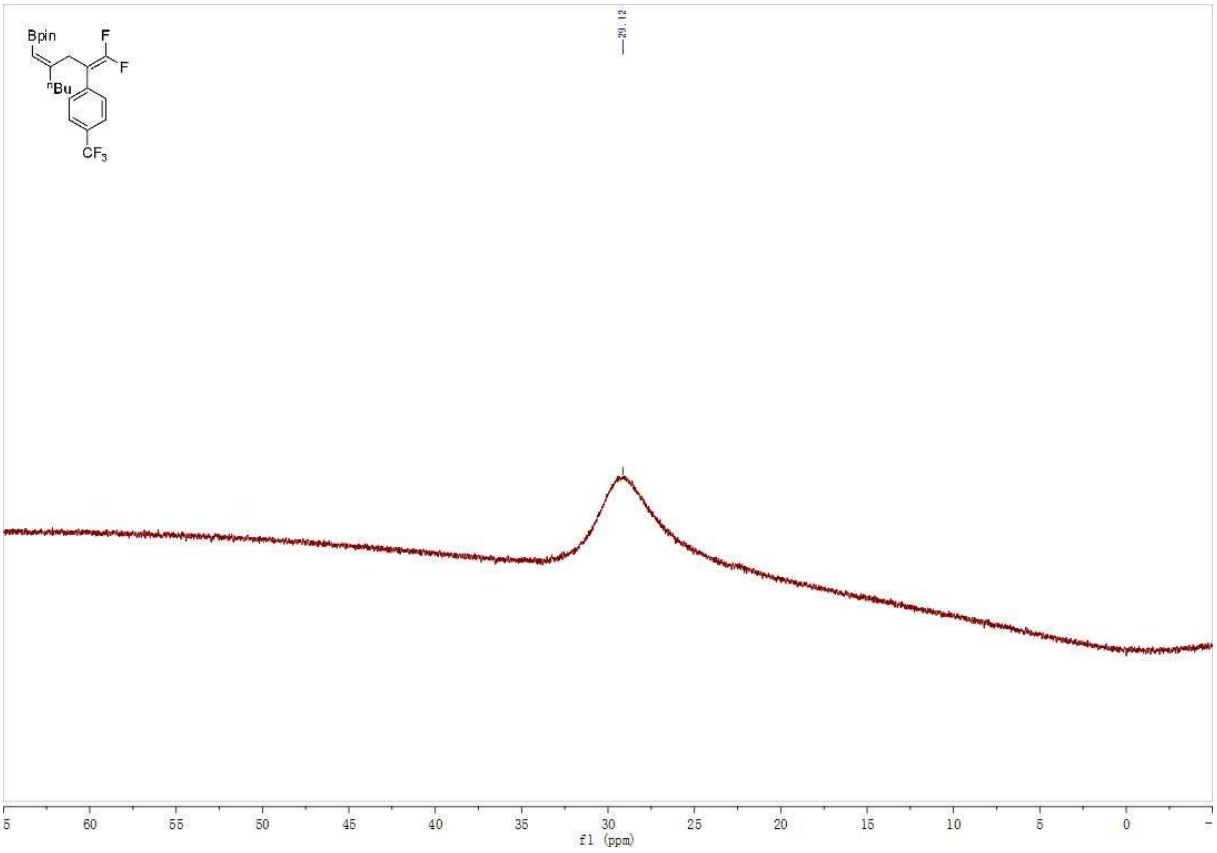
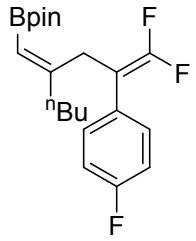
32.03
29.66
24.83
22.28
13.90
f1 (ppm)

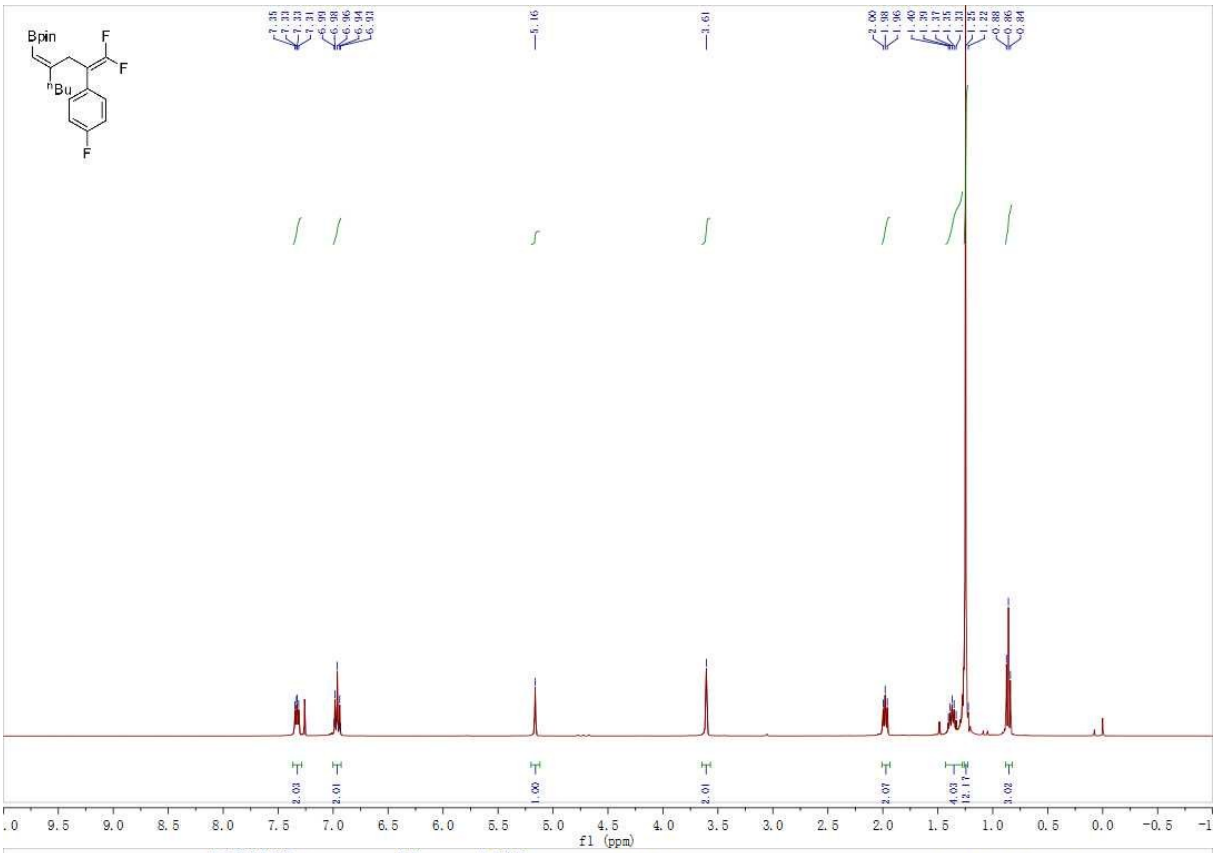

Bpin
F
F
nBu
CF3
62.66
89.36
89.46
89.66
89.76
f1 (ppm)

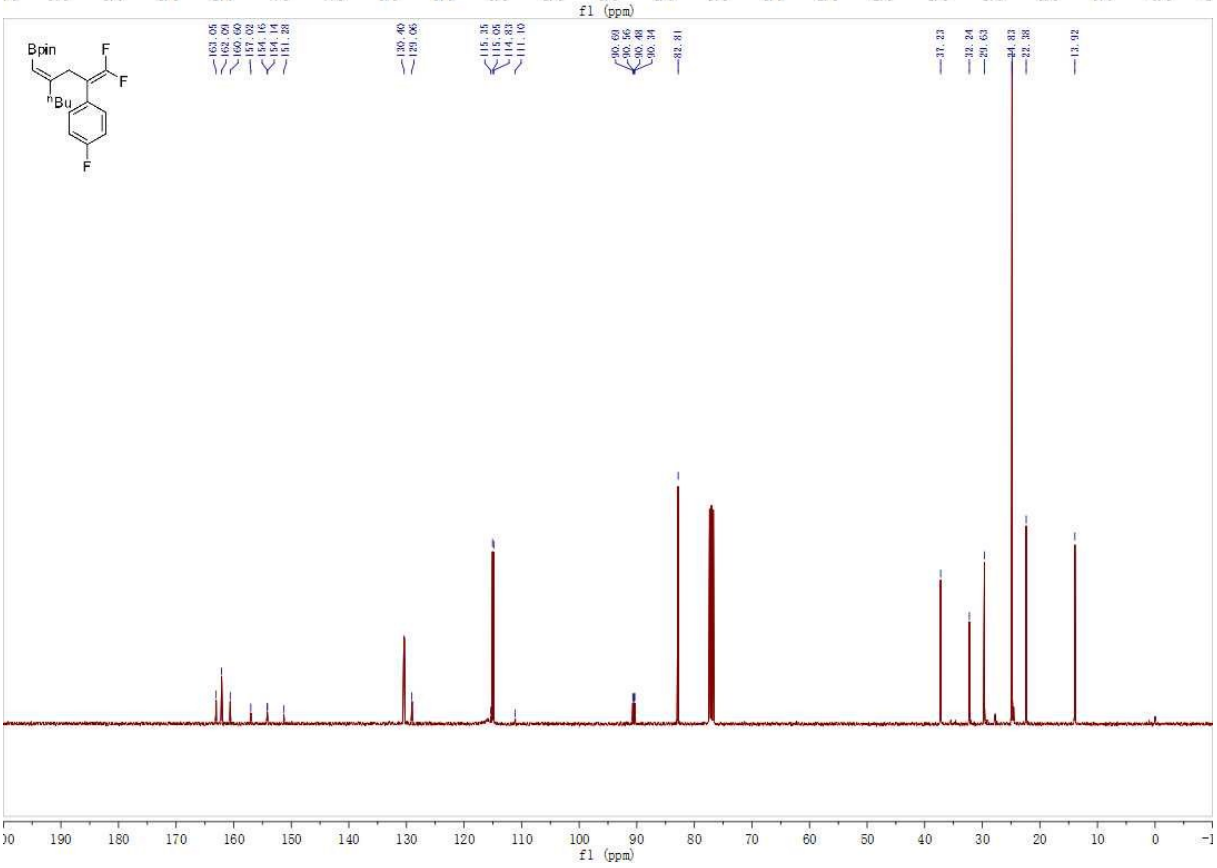


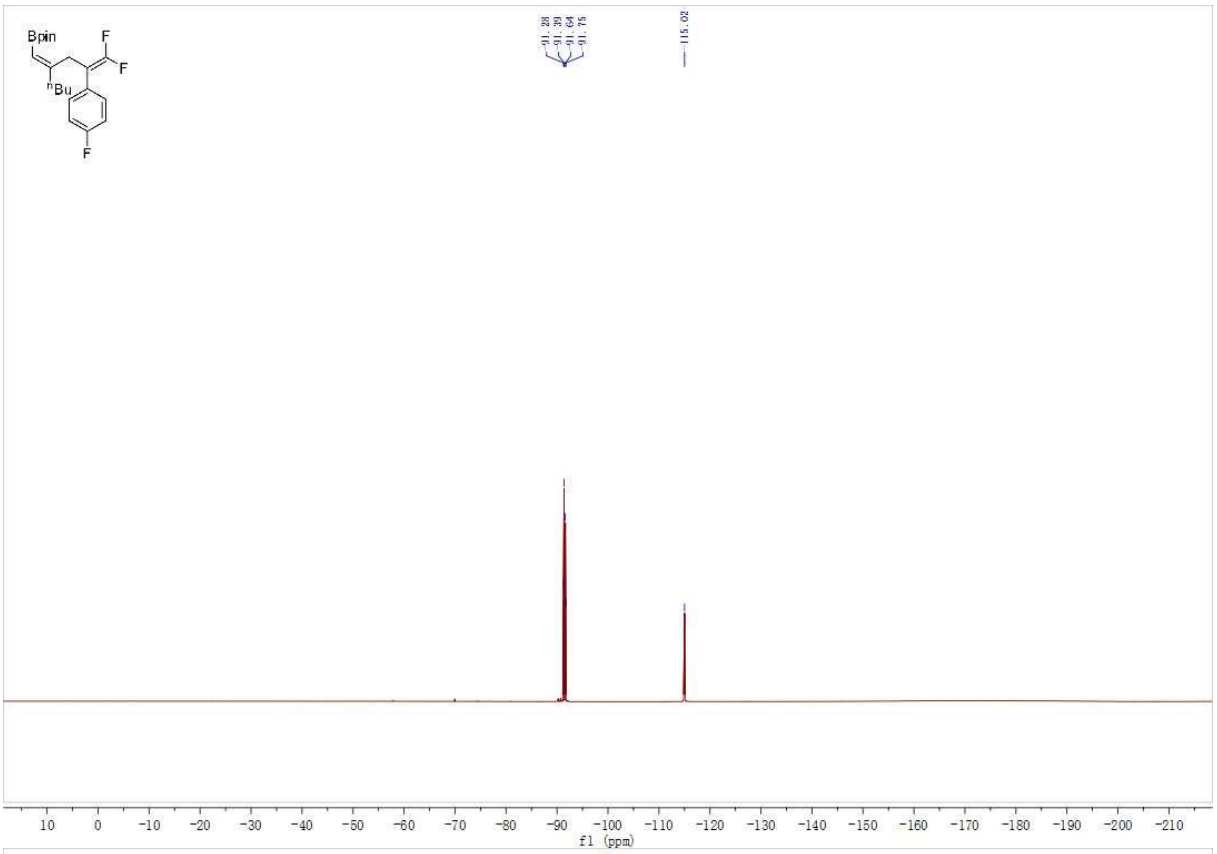
(Z)-2-(2-(3,3-difluoro-2-(4-fluorophenyl)allyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4f)

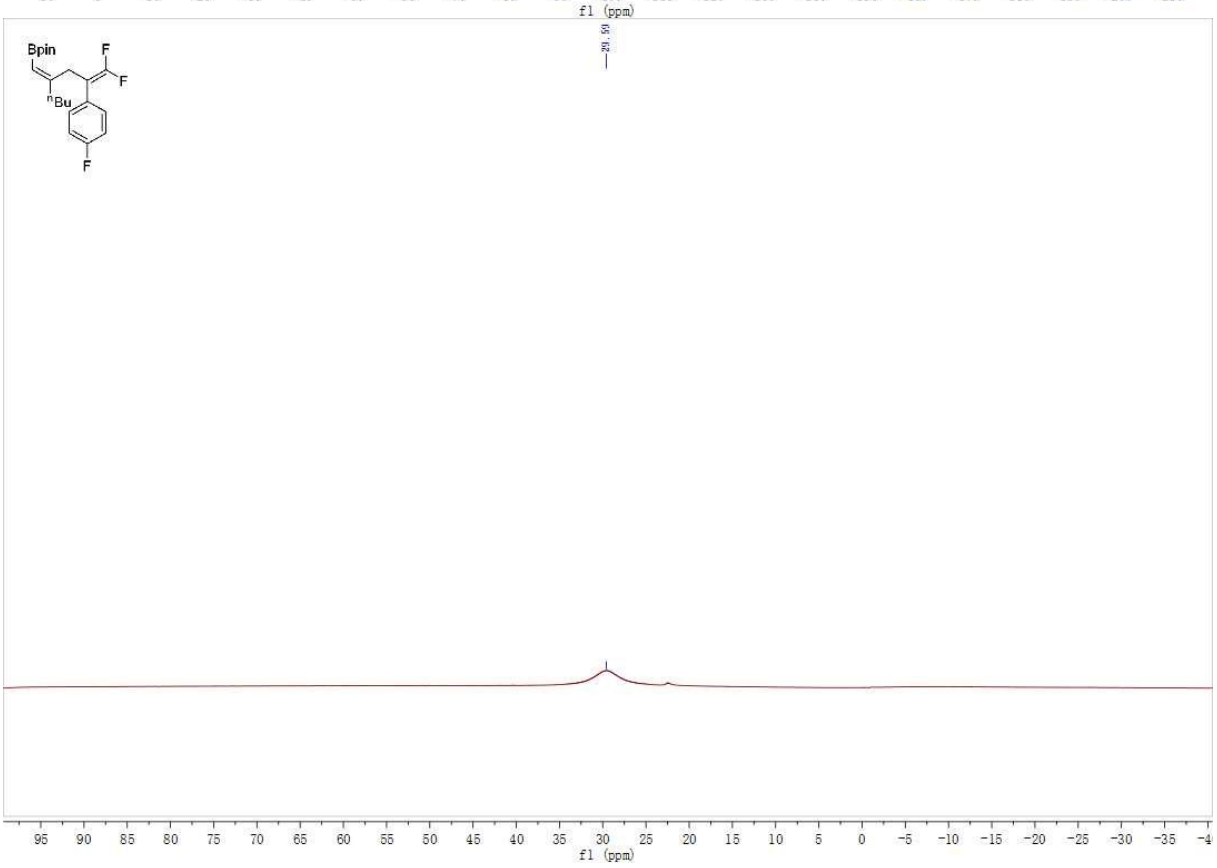


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (64.8 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.30 (m, 2H), 7.00 - 6.93 (m, 2H), 5.16 (s, 1H), 3.61 (s, 2H), 1.98 (t, *J* = 7.5Hz, 2H), 1.43 - 1.32 (m, 4H), 1.25 (s, 12H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.09 (s), 161.82 (d, *J* = 246.4 Hz), 154.15 (dd, *J* = 289.9, 287.8 Hz), 130.40 (s), 129.06 (s), 115.83 (s), 114.94 (d, *J* = 21.4 Hz), 90.52 (dd, *J* = 21.6, 13.5 Hz), 82.81 (s), 37.23 (s), 32.24 (s), 29.63 (s), 24.83 (s), 22.38 (s), 13.92 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.33 (d, *J* = 42.7 Hz), -91.69 (d, *J* = 42.7 Hz), -115.02. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.59. HRMS (ESI^+): Calcd for $C_{21}H_{28}BF_3O_2$ $[H]^+$: 381.2213, Found: 381.2213.

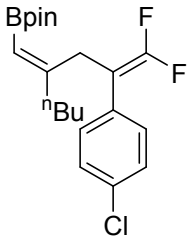

Bpin
F
F
nBu
F
7.35
7.33
7.33
7.31
6.99
6.98
6.96
6.94
6.93
5.16
3.61
2.00
1.98
1.96
1.40
1.29
1.27
1.25
1.22
0.88
0.86
0.84
2.03
2.01
1.00
2.01
2.07
4.03
12.17
3.02
f1 (ppm)


Bpin
F
F
nBu
F
163.05
162.09
160.60
157.02
154.16
154.14
151.28
130.40
129.06
115.35
115.05
114.83
111.10
90.69
90.58
90.48
90.34
82.81
37.23
32.24
29.63
24.83
22.38
13.92
f1 (ppm)

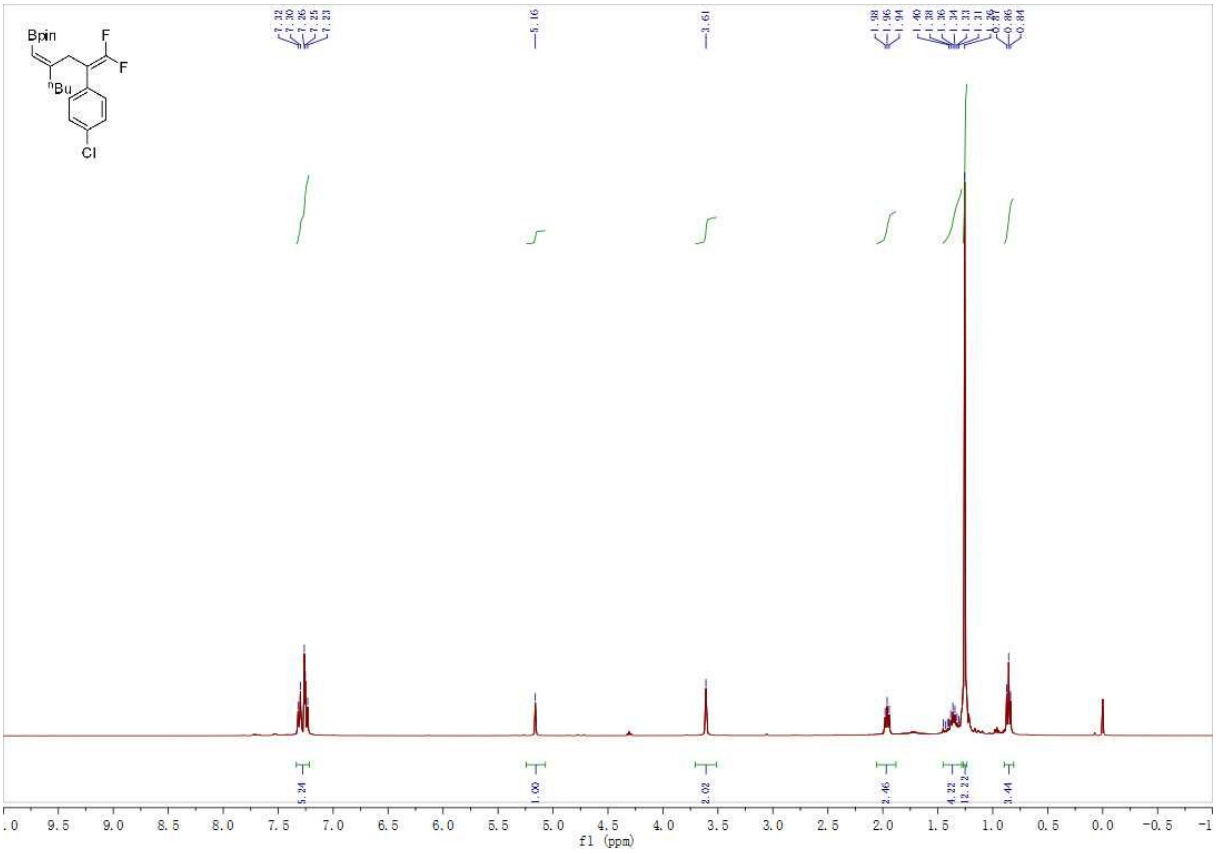

Bpin
F
F
nBu
F
-91.28
-91.39
-91.64
-91.75
-115.02
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

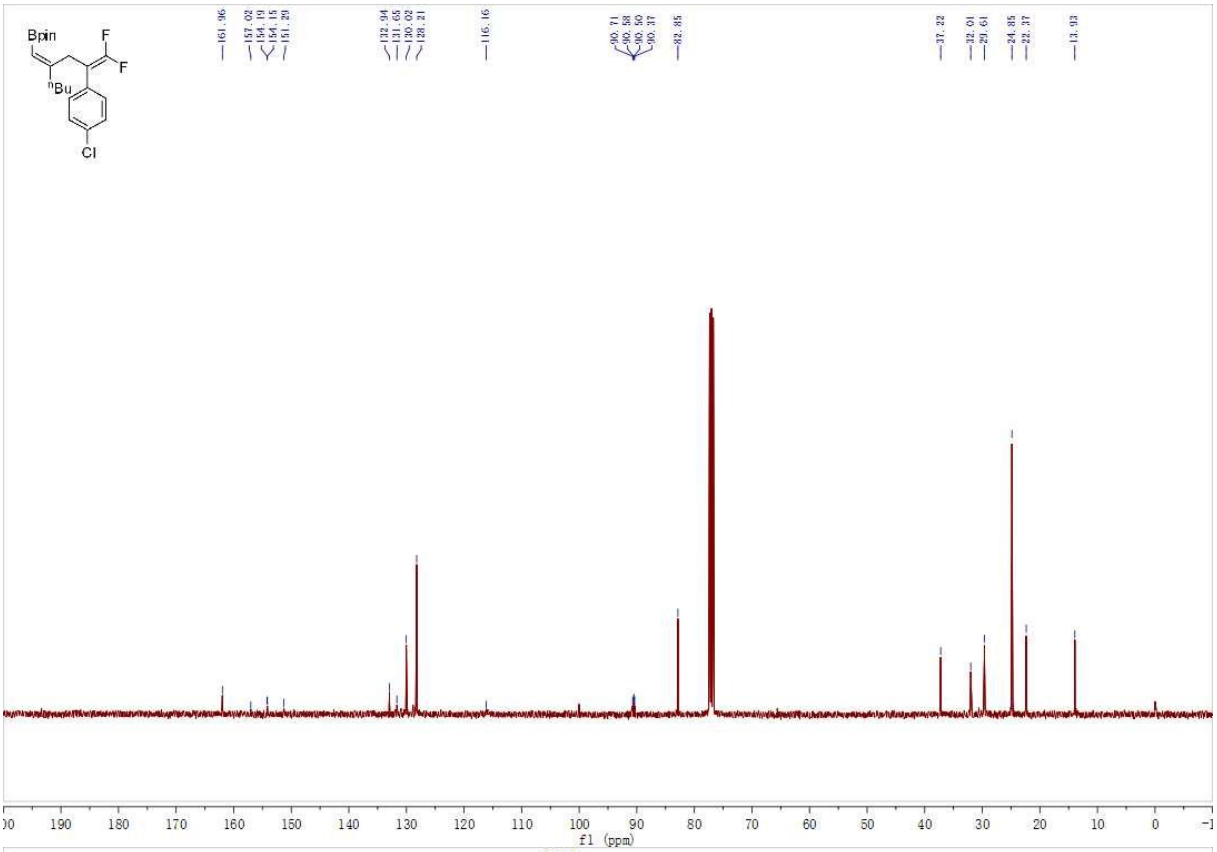

Bpin
F
F
nBu
F
29.59
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -4
f1 (ppm)

(Z)-2-(2-(2-(4-chlorophenyl)-3,3-difluoroallyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4g)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (59.5 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 - 6.98 (m, 4H), 5.16 (s, 1H), 3.61 (s, 2H), 1.99 – 1.92 (t, *J* = 7.5 Hz, 2H), 1.46 - 1.30 (m, 4H), 1.26 (s, 12H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.96, 154.16 (dd, *J* = 290.3, 286.5 Hz), 132.94, 131.65, 130.02, 128.21, 116.16, 90.54 (dd, *J* = 21.8, 13.1 Hz), 82.85, 37.22, 32.01, 29.61, 24.85, 22.37, 13.93. ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.40 (d, *J* = 40.8 Hz), -90.77 (d, *J* = 40.8 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.25. HRMS (ESI^+): Calcd for $C_{21}H_{28}BClF_2O_2$ $[H]^+$: 397.1917, Found: 397.1906.




Bpin
F
F
nBu
Cl
161.96
157.02
154.19
154.15
151.20
132.94
131.65
130.02
128.21
116.16
90.71
90.58
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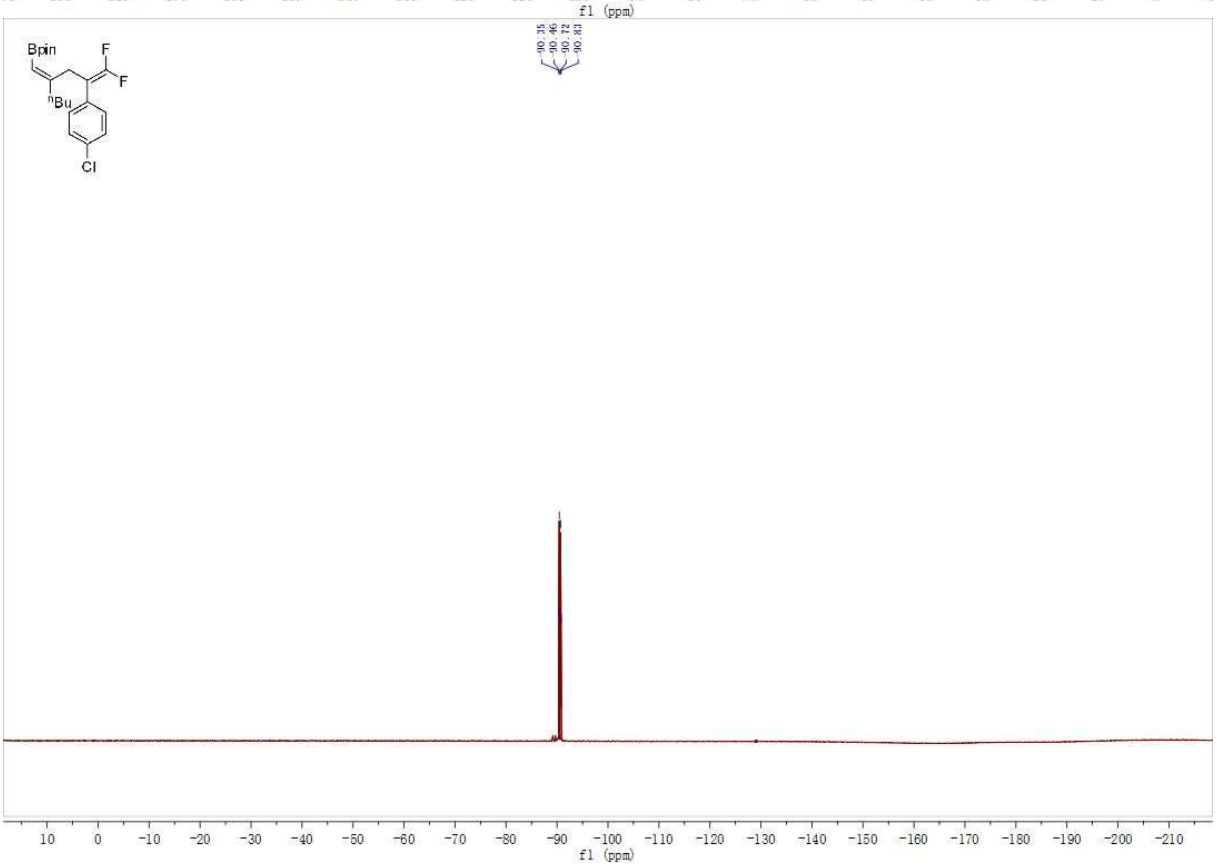
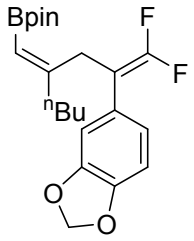
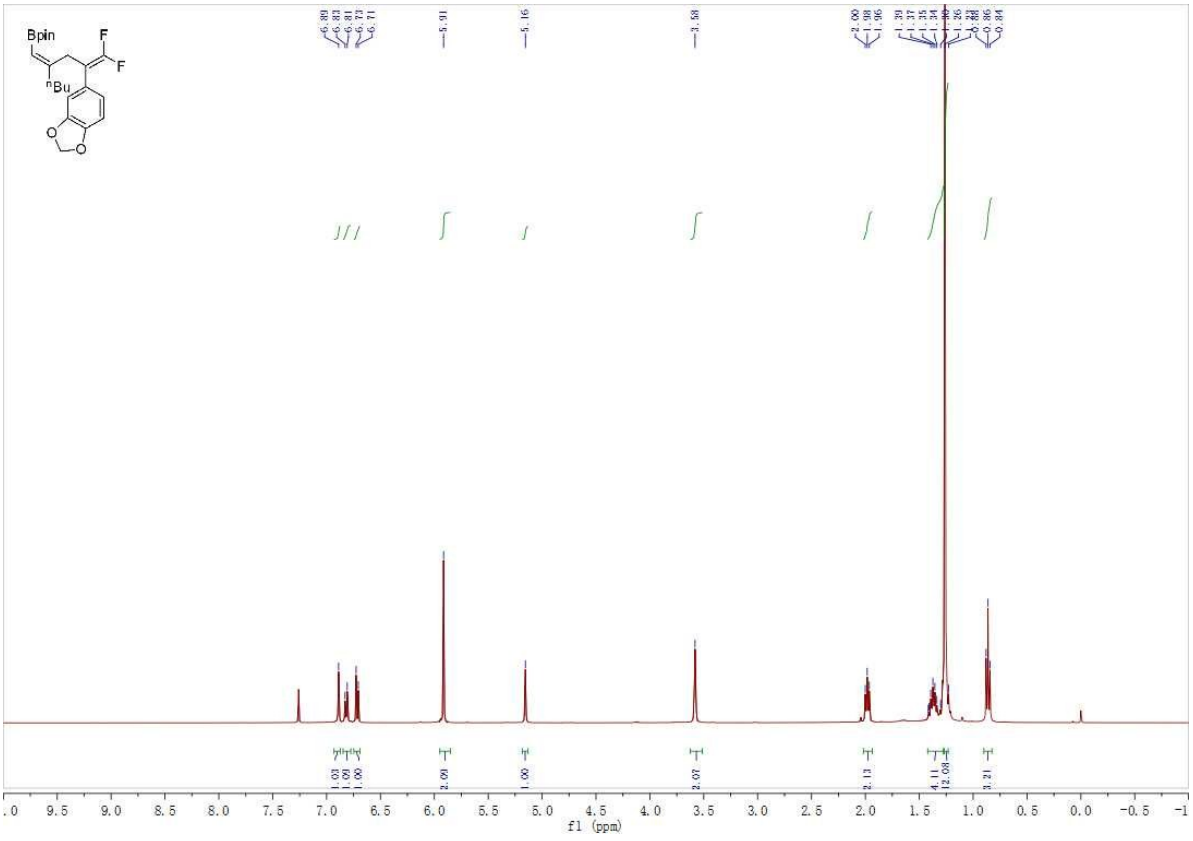
82.85
37.22
32.01
29.61
24.95
22.37
13.93
f1 (ppm)

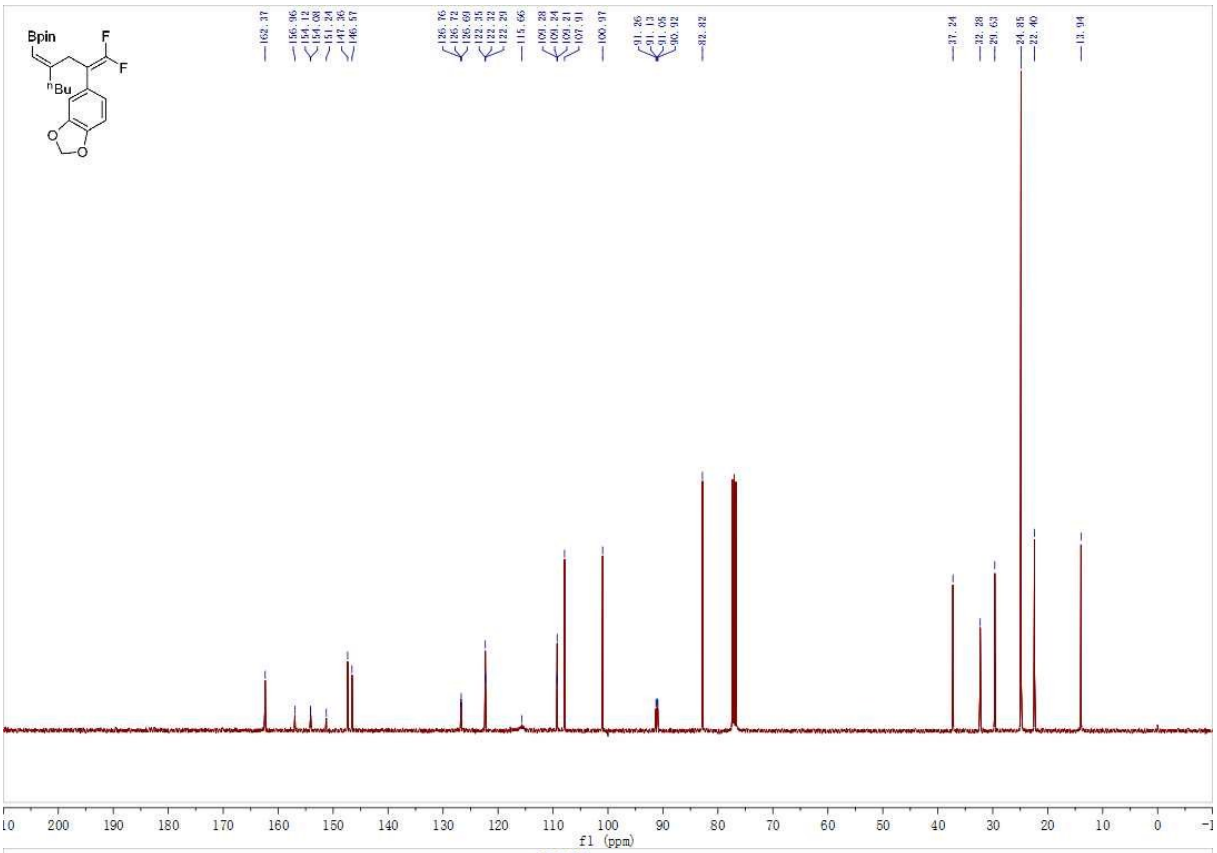

Bpin
F
F
nBu
Cl
90.35
90.46
90.72
90.83
f1 (ppm)

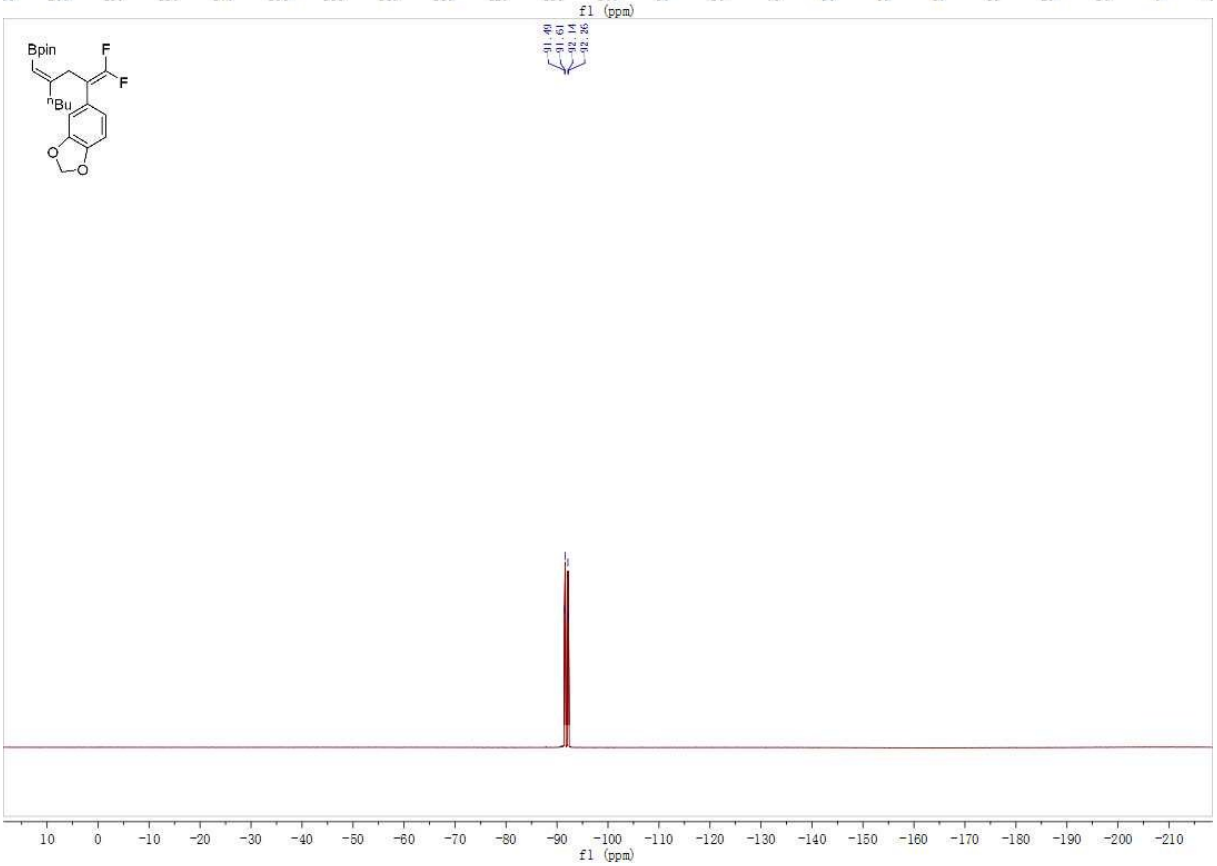
(Z)-2-(2-(2-(benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4h)

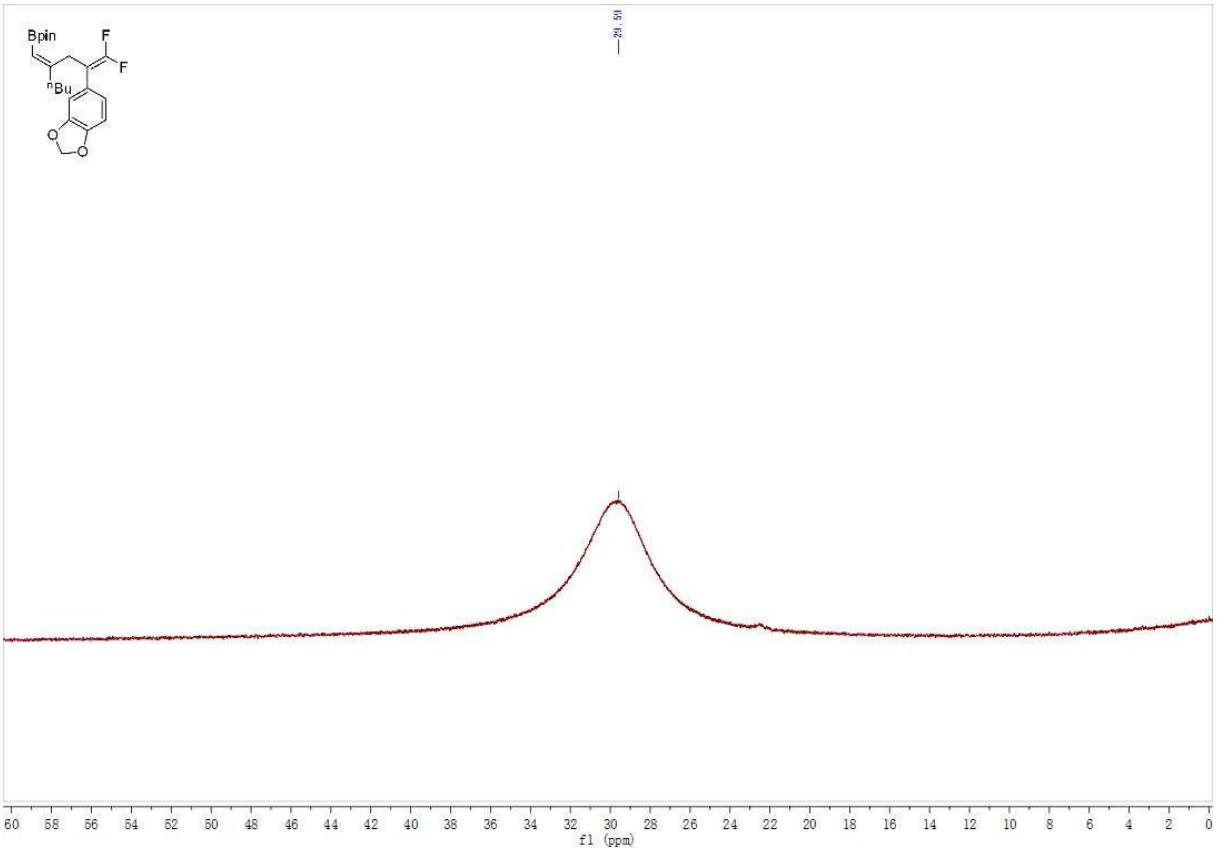


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (30:1) as thick oil (48.8 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 5.91 (s, 2H), 5.16 (s, 1H), 3.58 (s, 1H). 1.98 (t, *J* = 7.6 Hz, 2H), 1.43 - 1.30 (m, 4H), 1.26 (s, 12H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.37, 154.10 (dd, *J* = 289.6, 286.1 Hz), 147.36, 146.57, 126.72, 122.32 (t, *J* = 3.3 Hz), 115.69, 109.24, 107.91, 100.97, 91.09 (dd, *J* = 21.7, 13.3 Hz), 82.82, 37.24, 32.28, 29.63, 24.85, 22.40, 13.94. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.55 (d, *J* = 43.8 Hz), -92.20 (d, *J* = 43.8 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.59. HRMS (ESI^+): Calcd for $C_{22}H_{29}BF_2O_4$ $[H]^+$: 407.2205, Found: 407.2213.

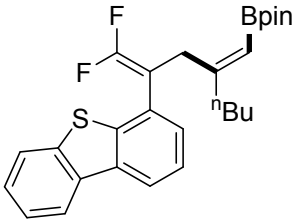



Bpin
F
F
nBu
O
O
162.37
156.96
154.12
154.08
151.24
147.36
146.57
126.76
126.72
126.69
122.35
122.32
122.29
115.66
109.28
109.24
109.21
107.91
100.97
91.26
91.13
91.05
90.92
82.82
37.24
32.28
29.63
24.95
22.40
13.94
f1 (ppm)

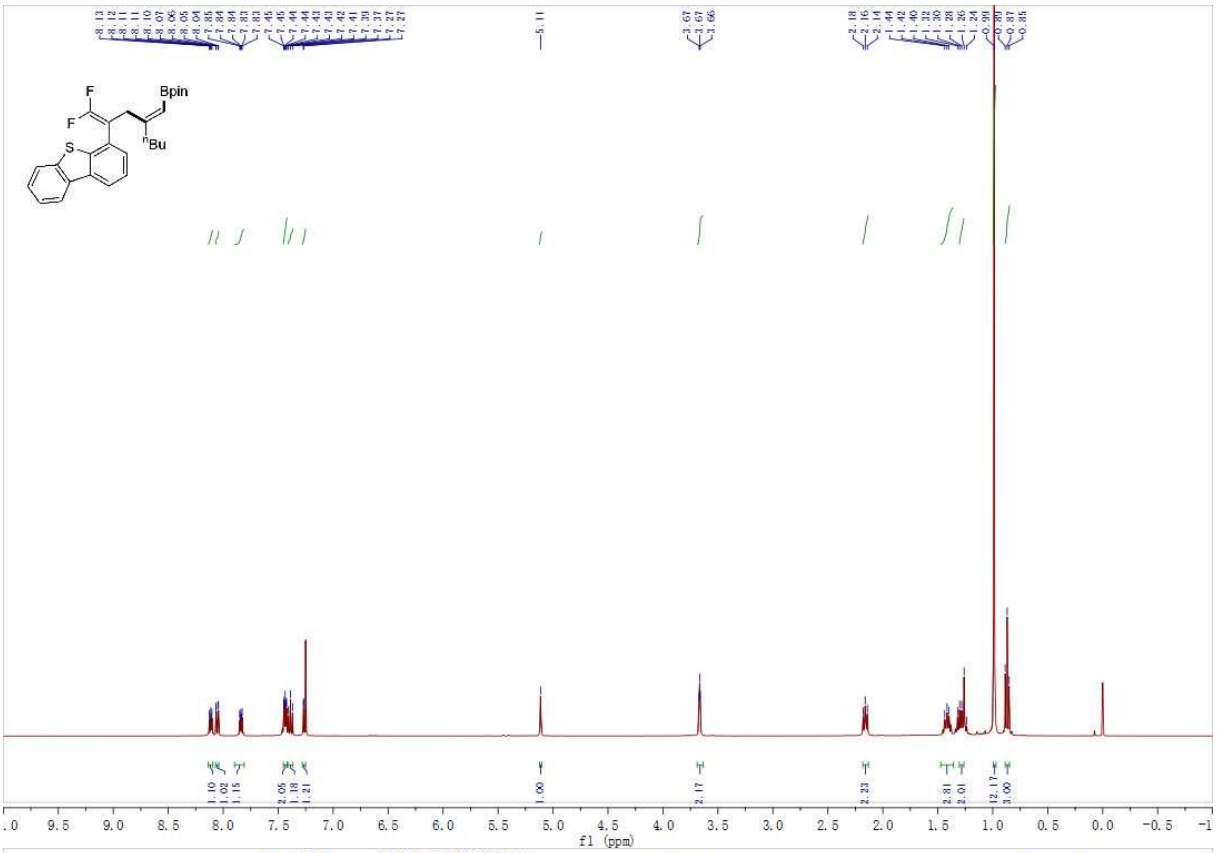

Bpin
F
F
nBu
O
O
91.49
91.61
92.14
92.26
f1 (ppm)

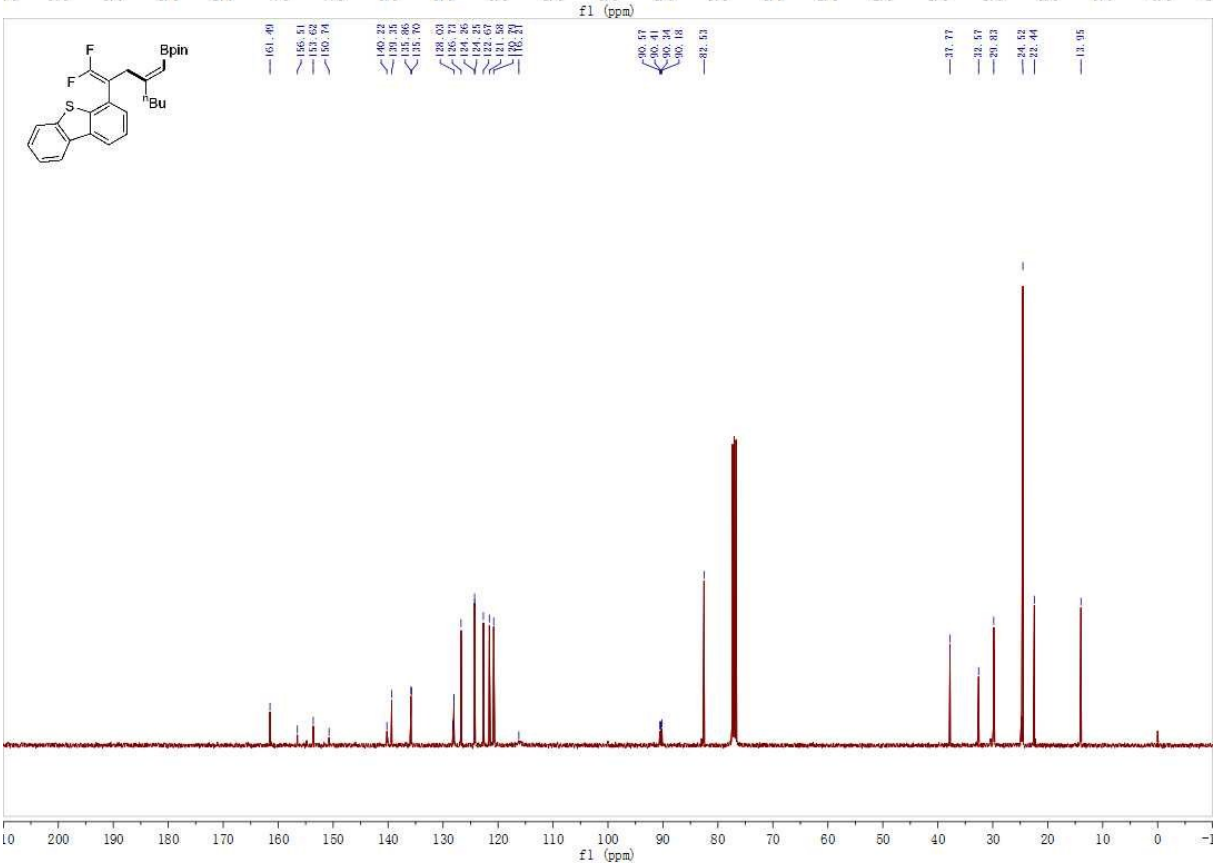


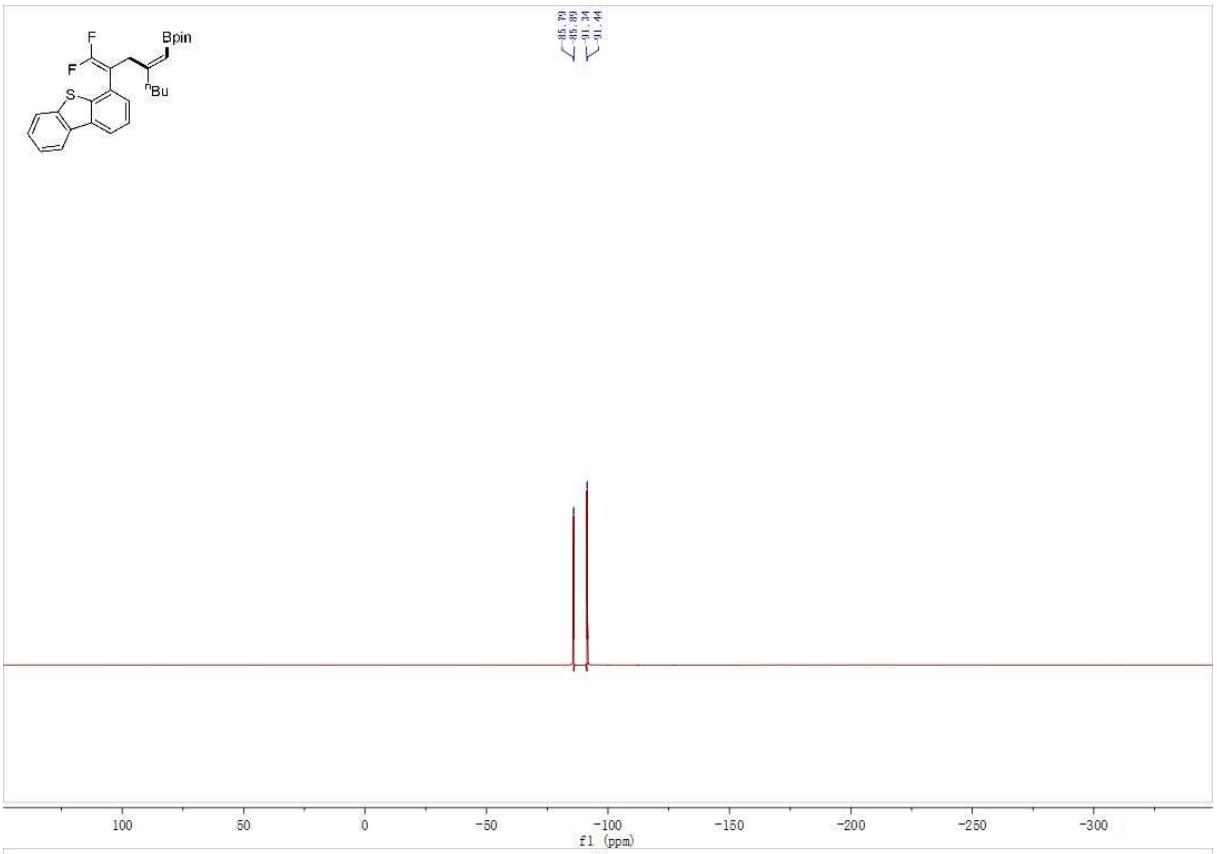
(Z)-2-(2-(2-(dibenzo[b,d]thiophen-4-yl)-3,3-difluoroallyl)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4i)

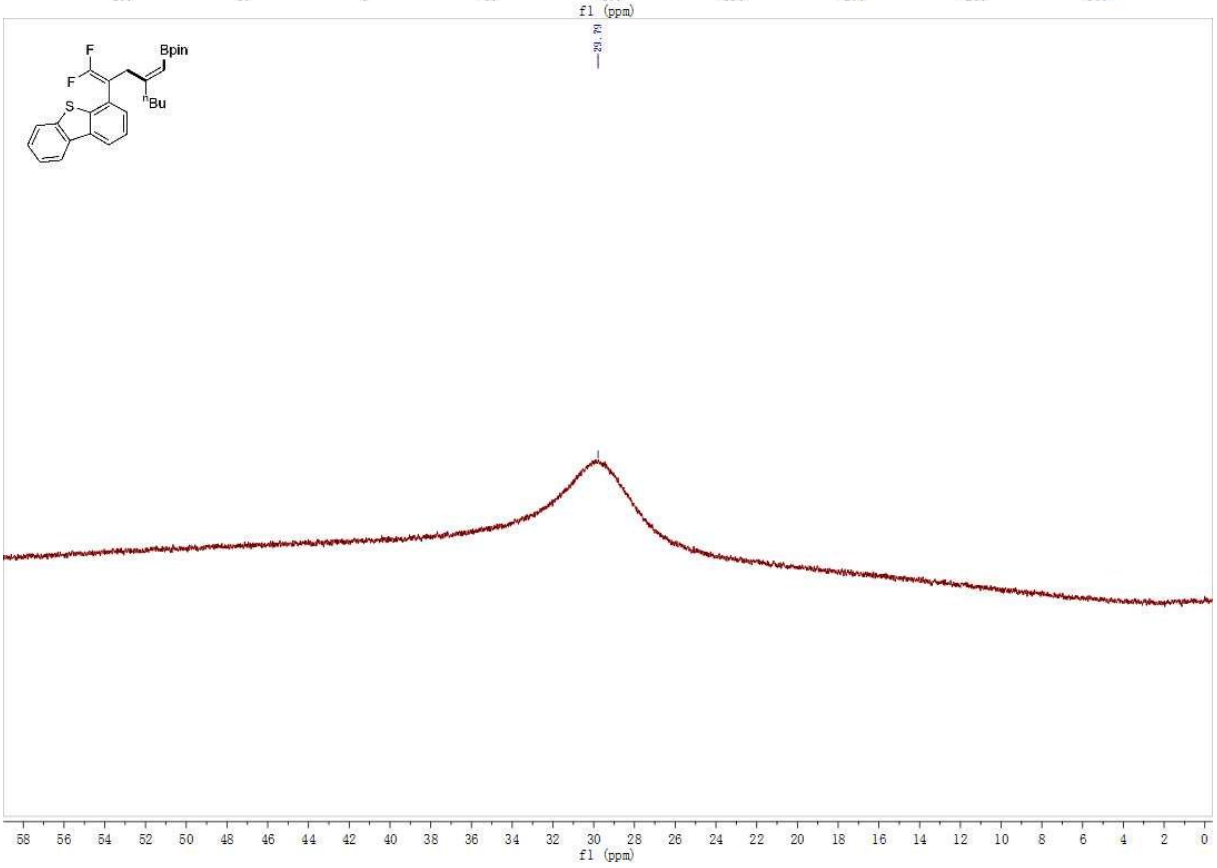


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (50:1) as white solid (73 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 - 8.08 (m, 1H), 8.07 - 8.04 (m, 1H), 7.89 - 7.81 (m, 1H), 7.47 - 7.42 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 1.0 Hz, 1H), 5.11 (s, 1H), 3.67 (s, 2H), 2.16 (t, *J* = 7.6 Hz, 2H), 1.46 - 1.35 (m, 2H), 1.34 - 1.21 (m, 2H), 0.99 (s, 12H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.49, 153.62 (dd, *J* = 288.86, 290.88 Hz), 140.22, 139.35, 135.86, 135.70, 128.20, 128.03, 126.73, 124.26, 122.67, 121.58, 120.79, 116.21, 90.37 (dd, *J* = 23.1, 16.1 Hz), 82.53, 37.77, 32.57, 29.83, 24.52, 22.44, 13.95. ^{19}F NMR (377 MHz, $CDCl_3$) δ -85.84 (d, *J* = 37.3 Hz), -91.39 (d, *J* = 37.3 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.79. HRMS (ESI^+): Calcd for $C_{27}H_{31}BF_2O_2S$ $[Na]^+$: 491.2004, Found: 491.1993.

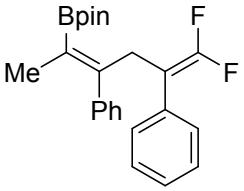

F
F
S
Bpin
nBu
f1 (ppm)


F
F
S
Bpin
nBu
f1 (ppm)

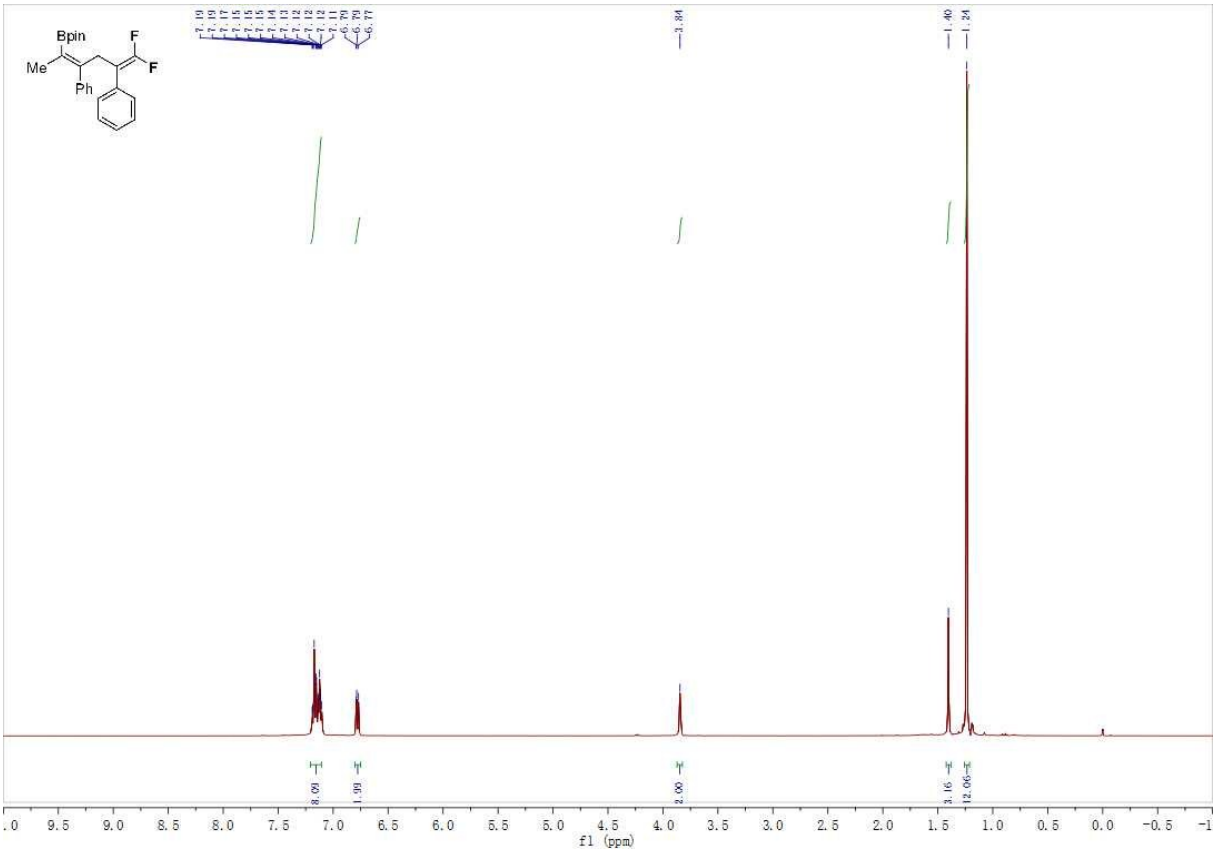

F
F
Bpin
S
nBu
-85.79
-85.89
-91.34
-91.44
100
50
0
-50
-100
-150
-200
-250
-300
f1 (ppm)

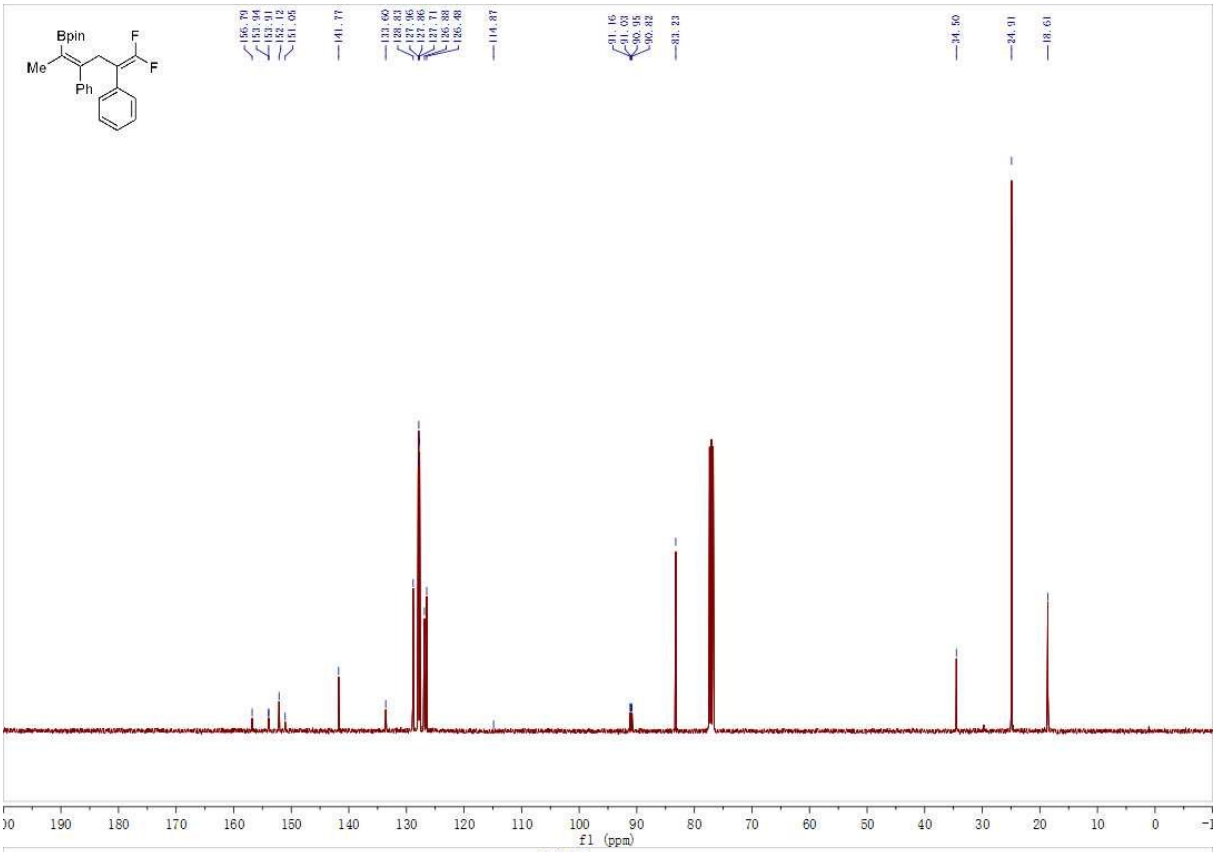

F
F
Bpin
S
nBu
29.79
58
56
54
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
f1 (ppm)

(Z)-2-(6,6-difluoro-3,5-diphenylhexa-2,5-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4j)



Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (44.5 mg, 56 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 6.99 (m, 8H), 6.84 - 6.68 (m, 2H), 3.84 (s, 2H), 1.40 (s, 3H), 1.24 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.92 (dd, J = 290.2, 287.0 Hz), 152.12, 141.77, 133.60, 128.83, 127.96, 127.86, 127.71,126.88, 126.48, 114.87, 90.99 (dd, J = 20.7, 13.1 Hz), 83.23, 34.50, 24.91, 18.61. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.23 (d, J = 40.8 Hz), -92.29 (d, J = 40.8 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.96. HRMS (ESI$^+$): Calcd for $C_{24}H_{27}BF_2O_2$ [H]$^+$: 397.2150, Found: 397.2160.




Bpin
F
Me
F
Ph
156.79
153.94
153.91
152.12
151.66
141.77
133.60
128.83
127.96
127.86
127.71
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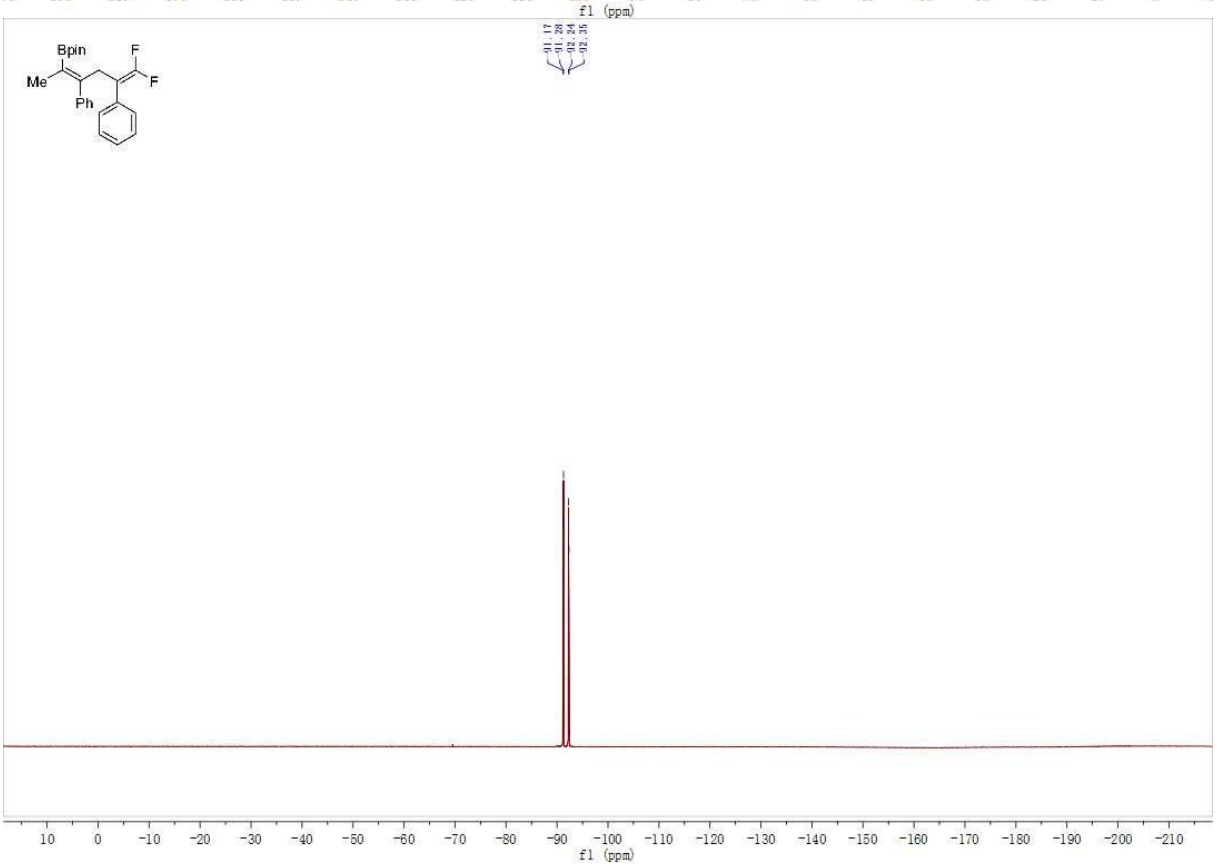
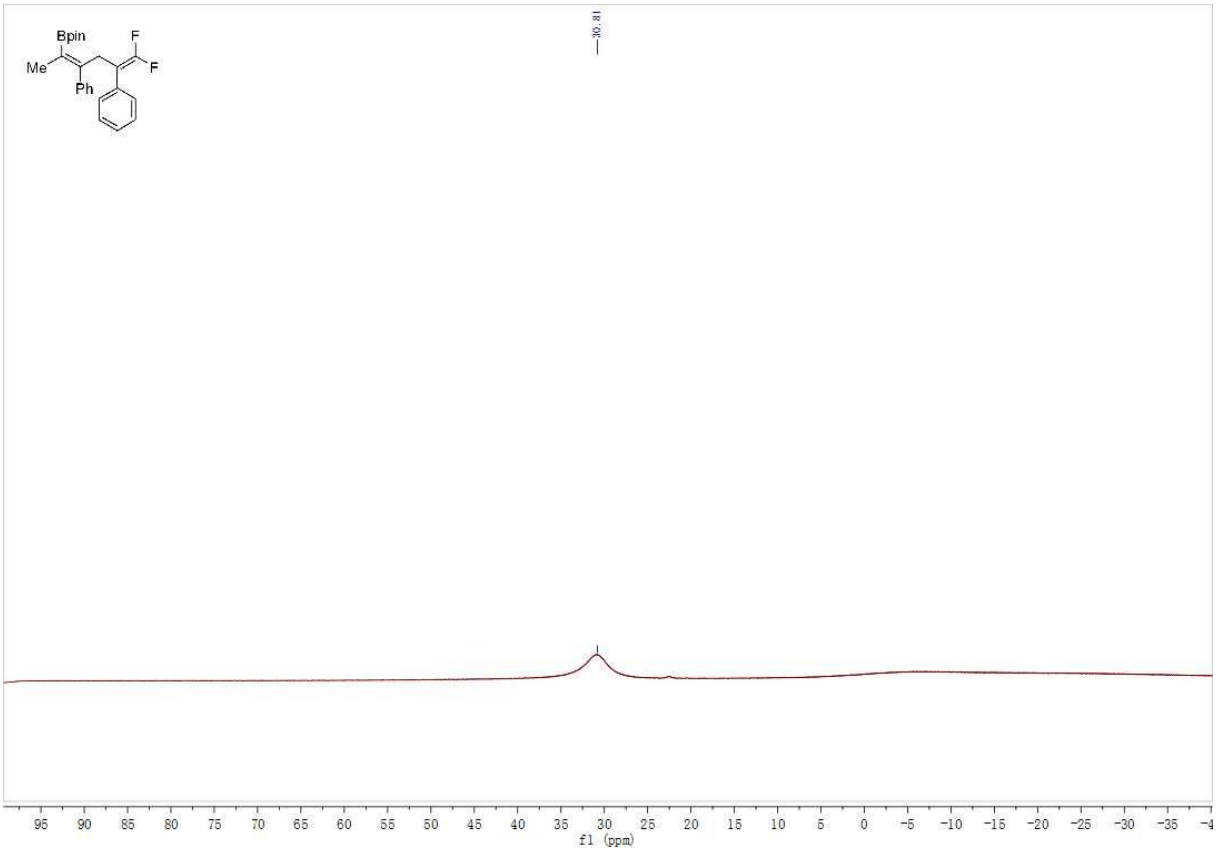
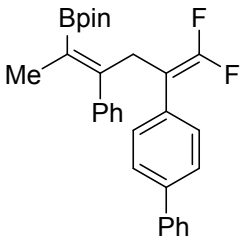
90.95
90.82
83.23
34.50
24.91
18.61
f1 (ppm)

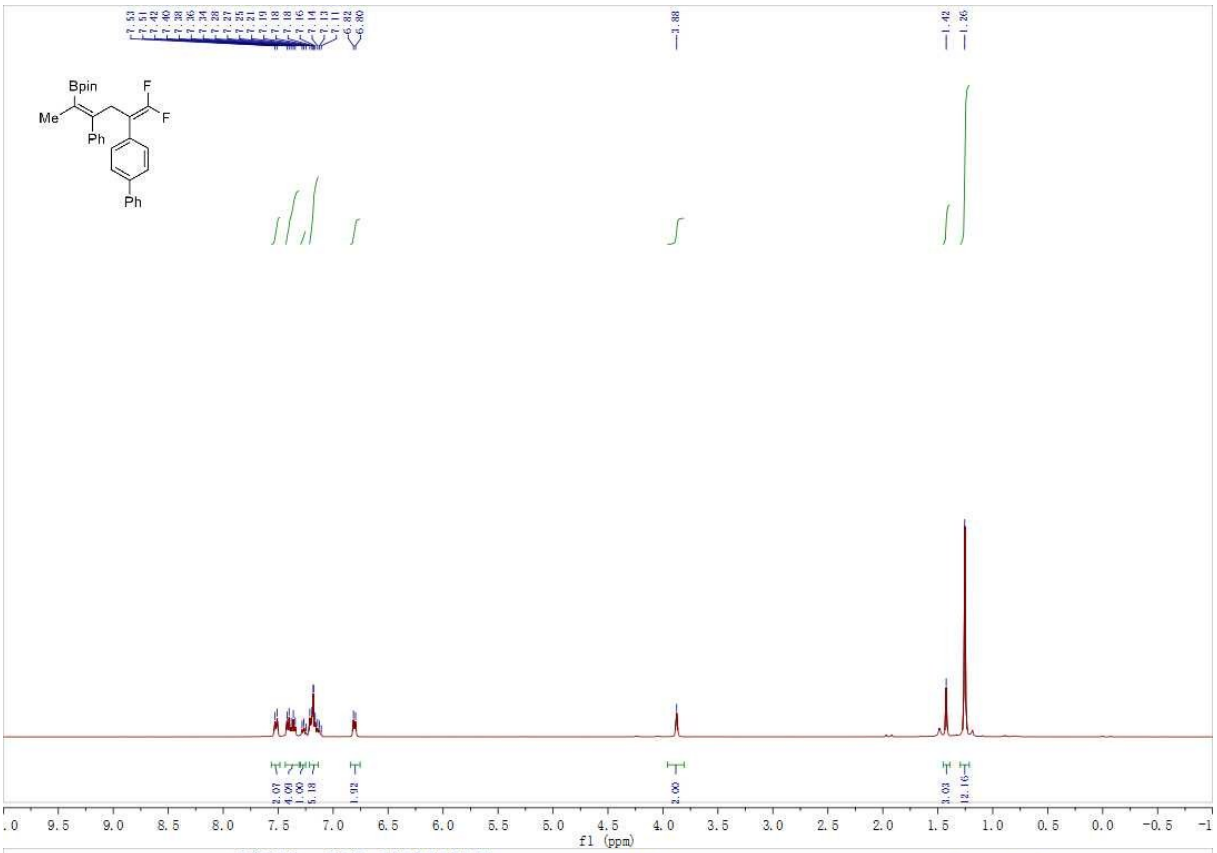

Bpin
F
Me
F
Ph
-91.17
-91.28
-92.24
-92.35
f1 (ppm)

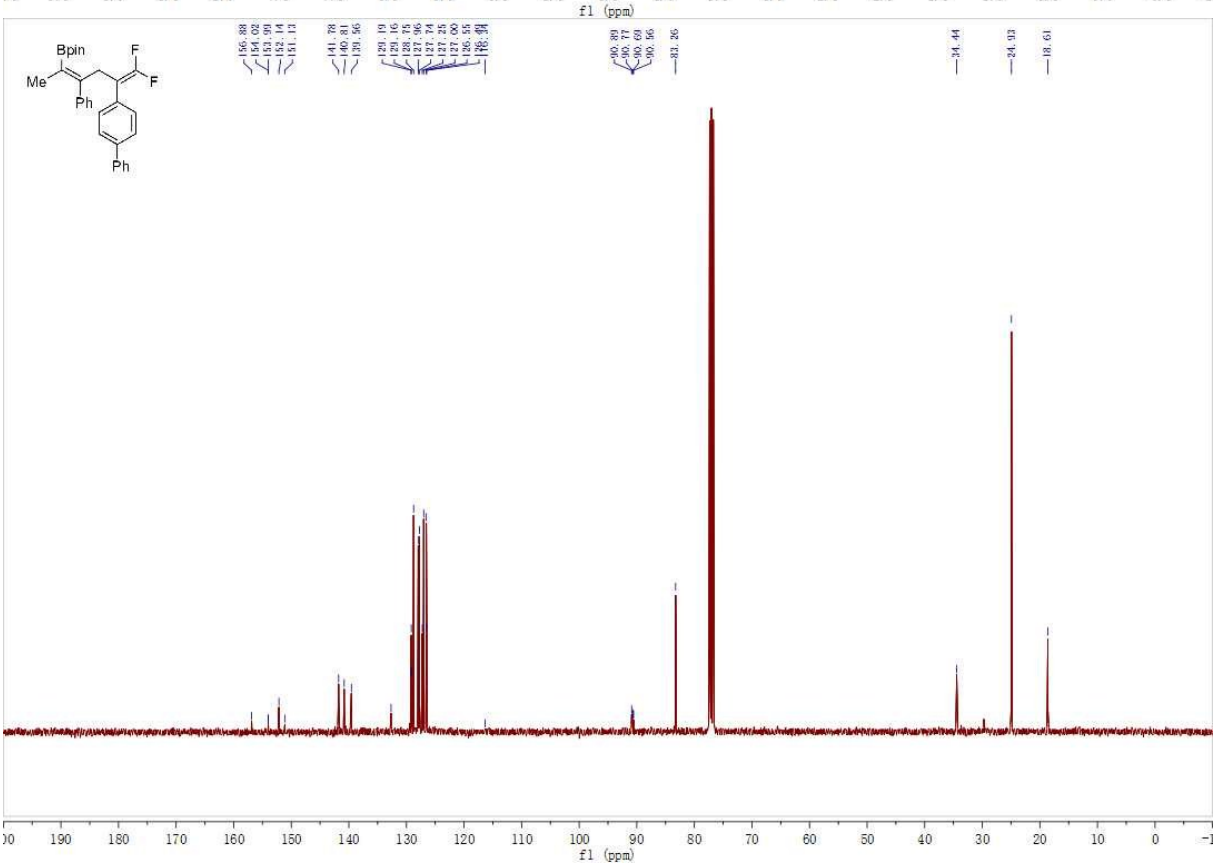


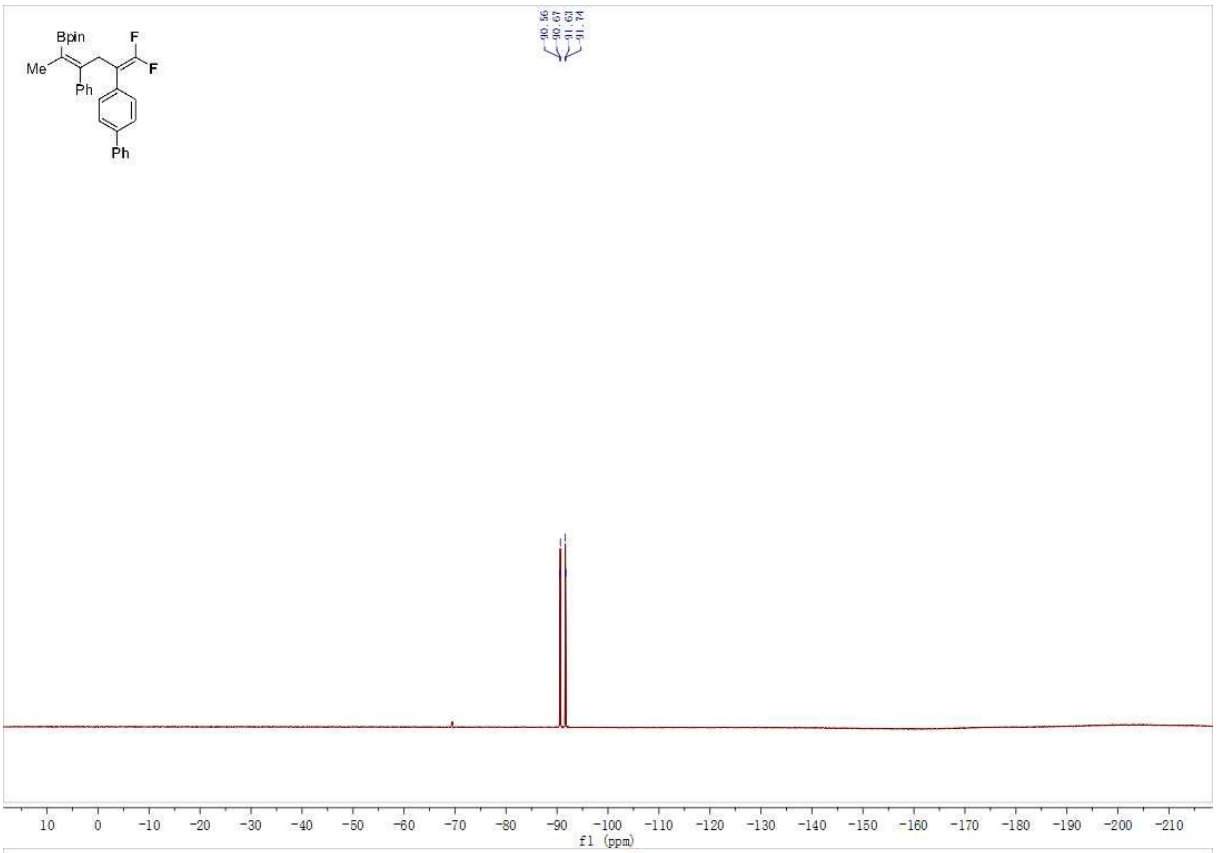
(Z)-2-(5-([1,1'-biphenyl]-4-yl)-6,6-difluoro-3-phenylhexa-2,5-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4k)

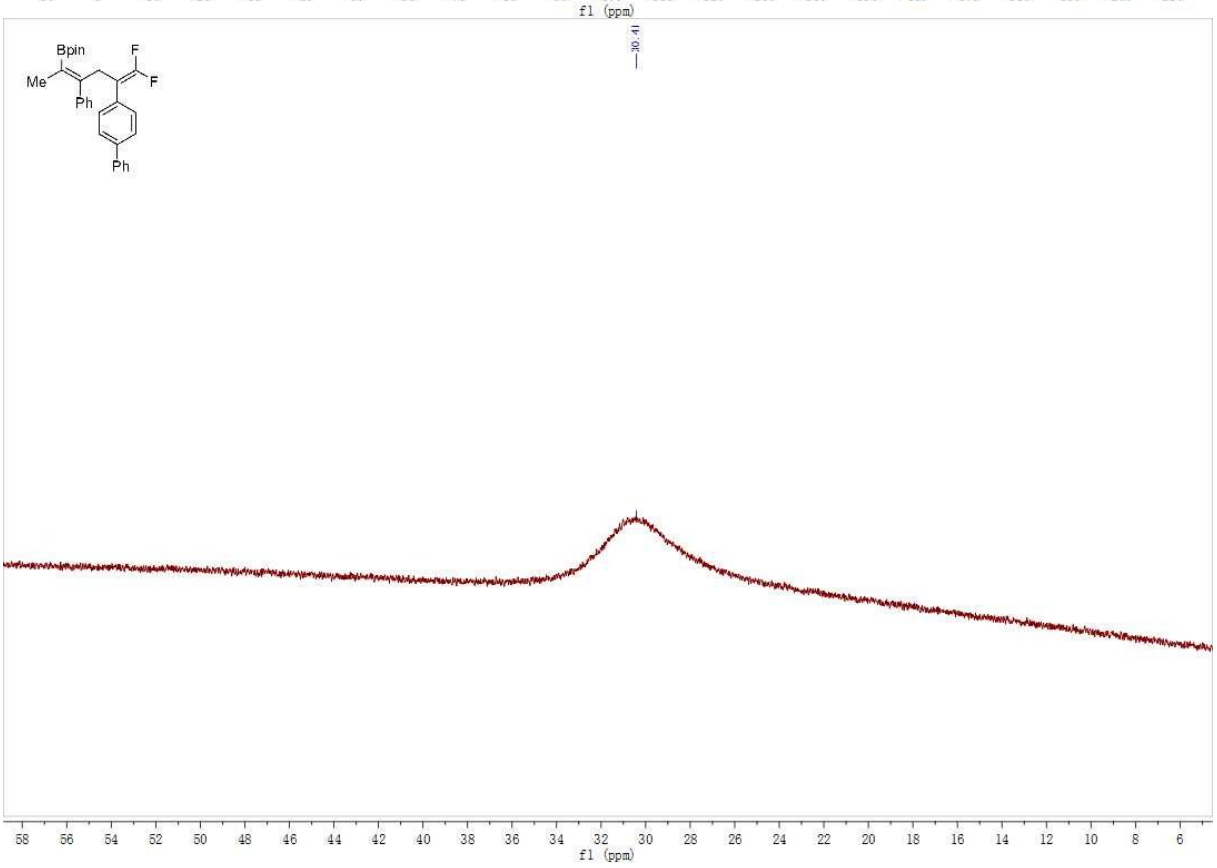


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as white solid (70 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.44 - 7.31 (m, 4H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.21 - 7.14 (m, 5H), 6.81 (d, *J* = 7.6 Hz, 2H), 3.88 (s, 2H), 1.42 (s, 3H), 1.26 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.01 (dd, *J* = 290.6, 287.6 Hz), 152.14, 141.78, 140.81, 139.56, 132.67, 129.16, 128.75, 127.96, 127.74, 127.25, 127.00, 126.55, 126.49, 116.34, 90.73 (dd, *J* = 20.8, 12.9 Hz), 83.26, 34.44, 24.93, 18.61. ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.61 (d, *J* = 40.0 Hz), -91.69 (d, *J* = 40.0 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.41. HRMS (ESI^+): Calcd for $C_{30}H_{31}BF_2O_2$ $[H]^+$: 473.2463, Found: 473.2466.

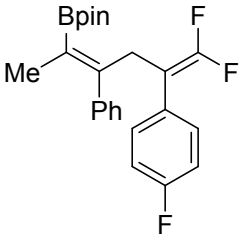

Bpin
F
F
Me
Ph
Ph
f1 (ppm)


Bpin
F
F
Me
Ph
Ph
f1 (ppm)

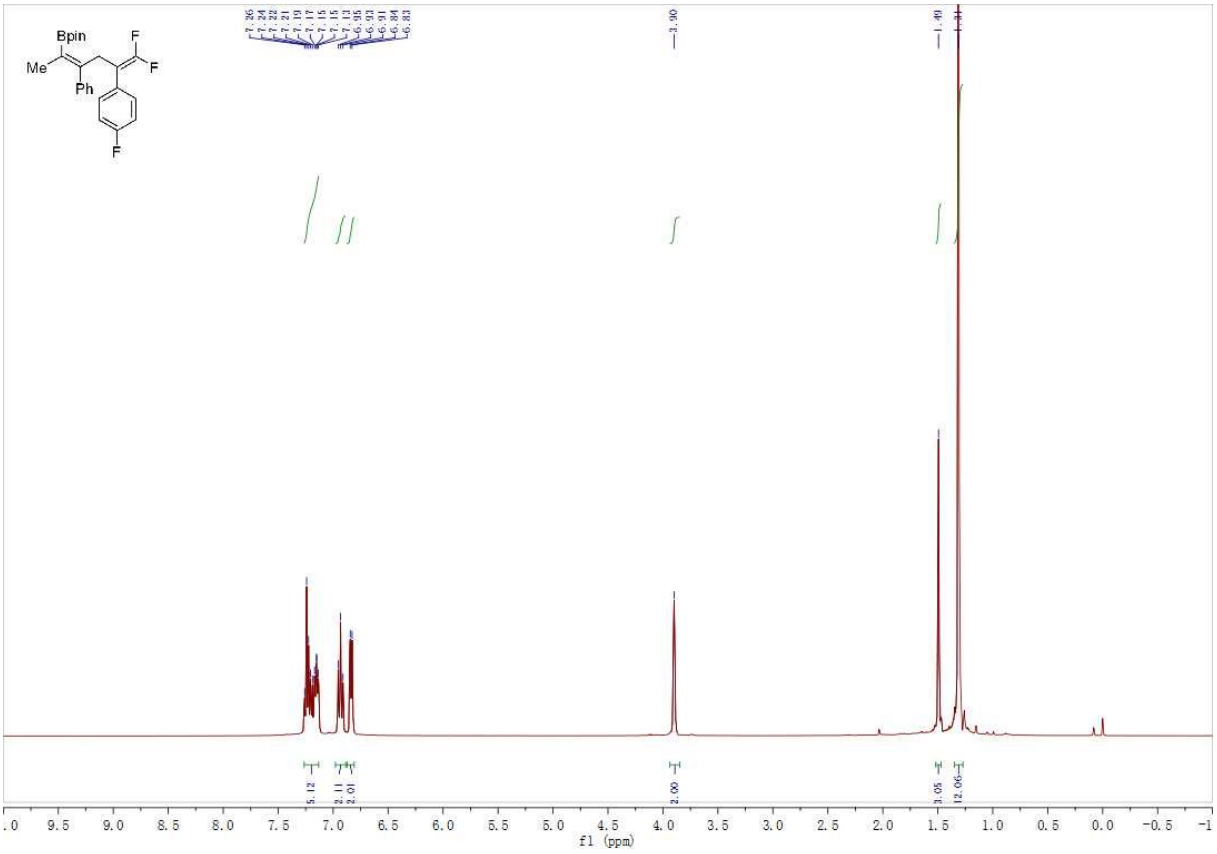

Bpin
F
Me
F
Ph
Ph
-90.56
-90.67
-91.63
-91.74
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

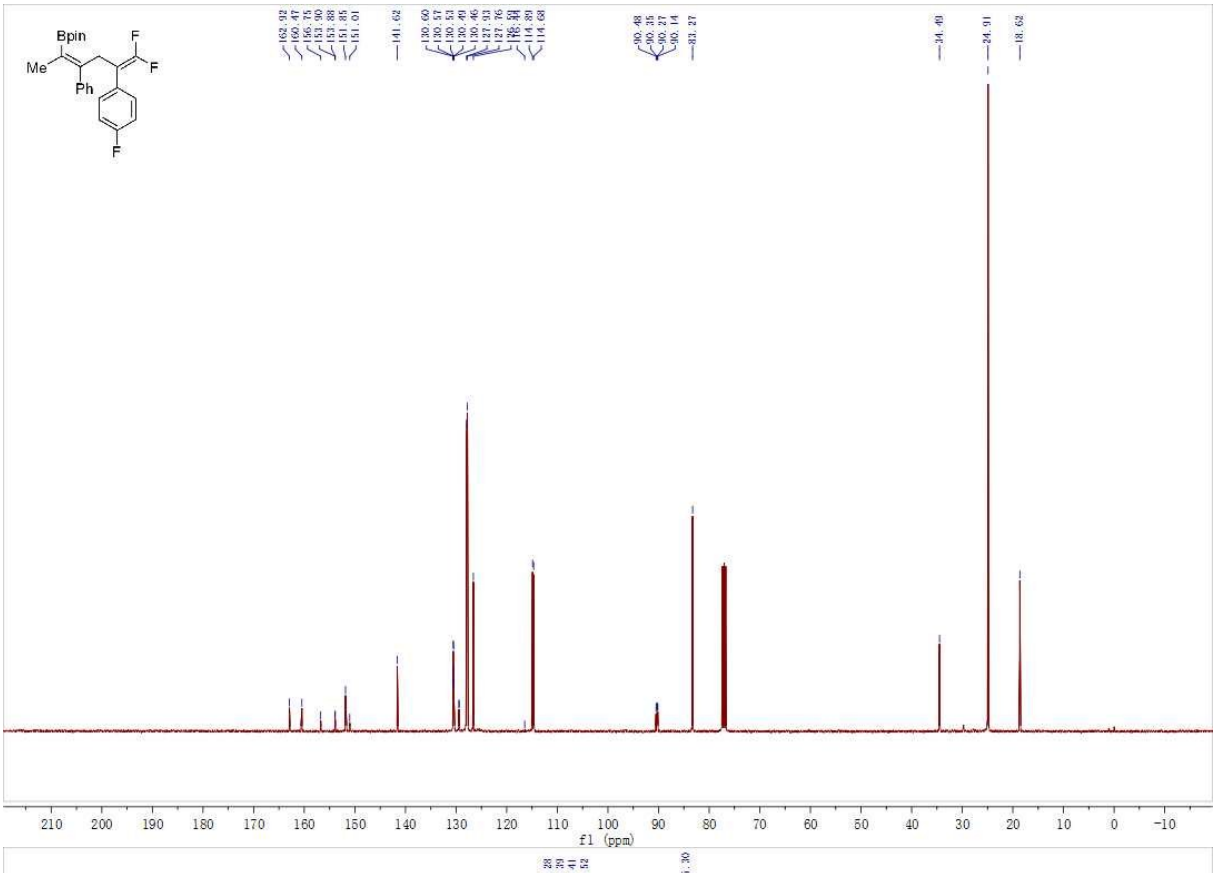

Bpin
F
Me
F
Ph
Ph
30.41
58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6
f1 (ppm)

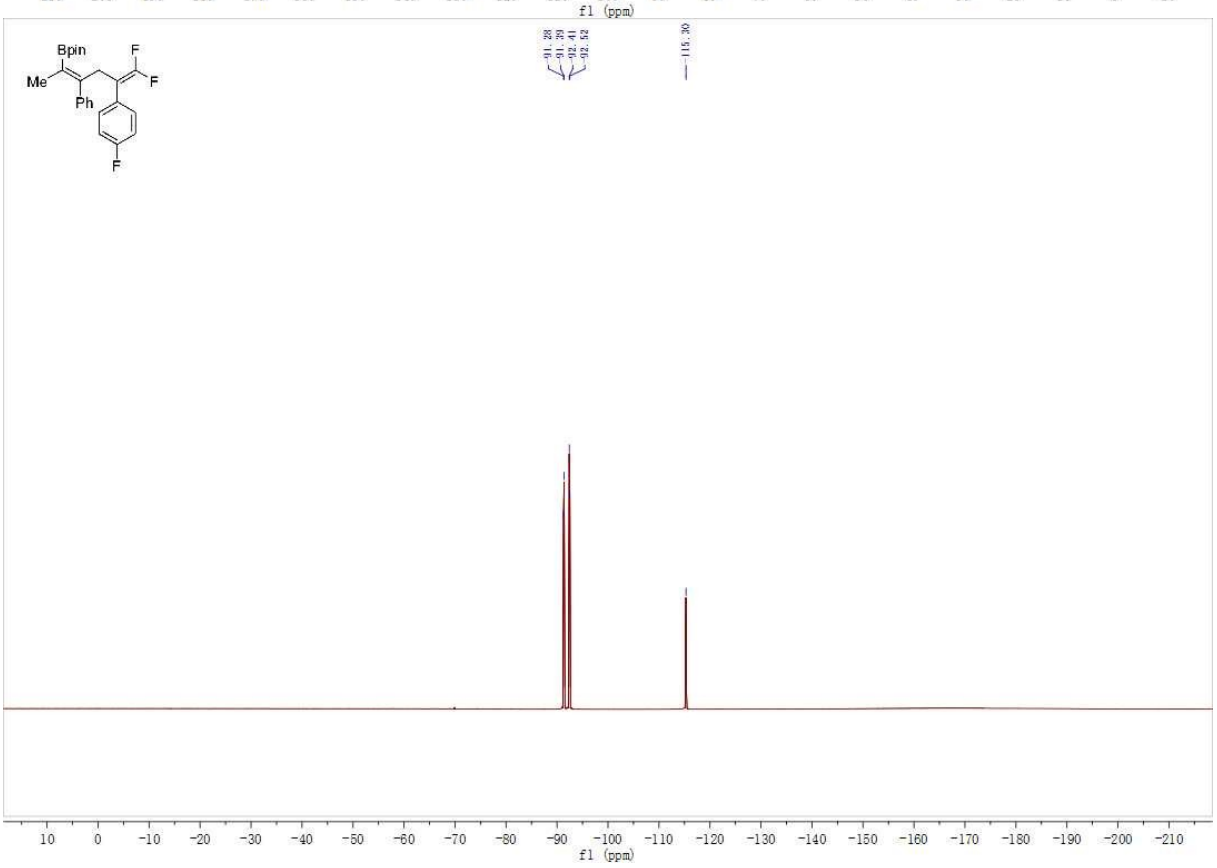
(Z)-2-(6,6-difluoro-5-(4-fluorophenyl)-3-phenylhexa-2,5-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4l)

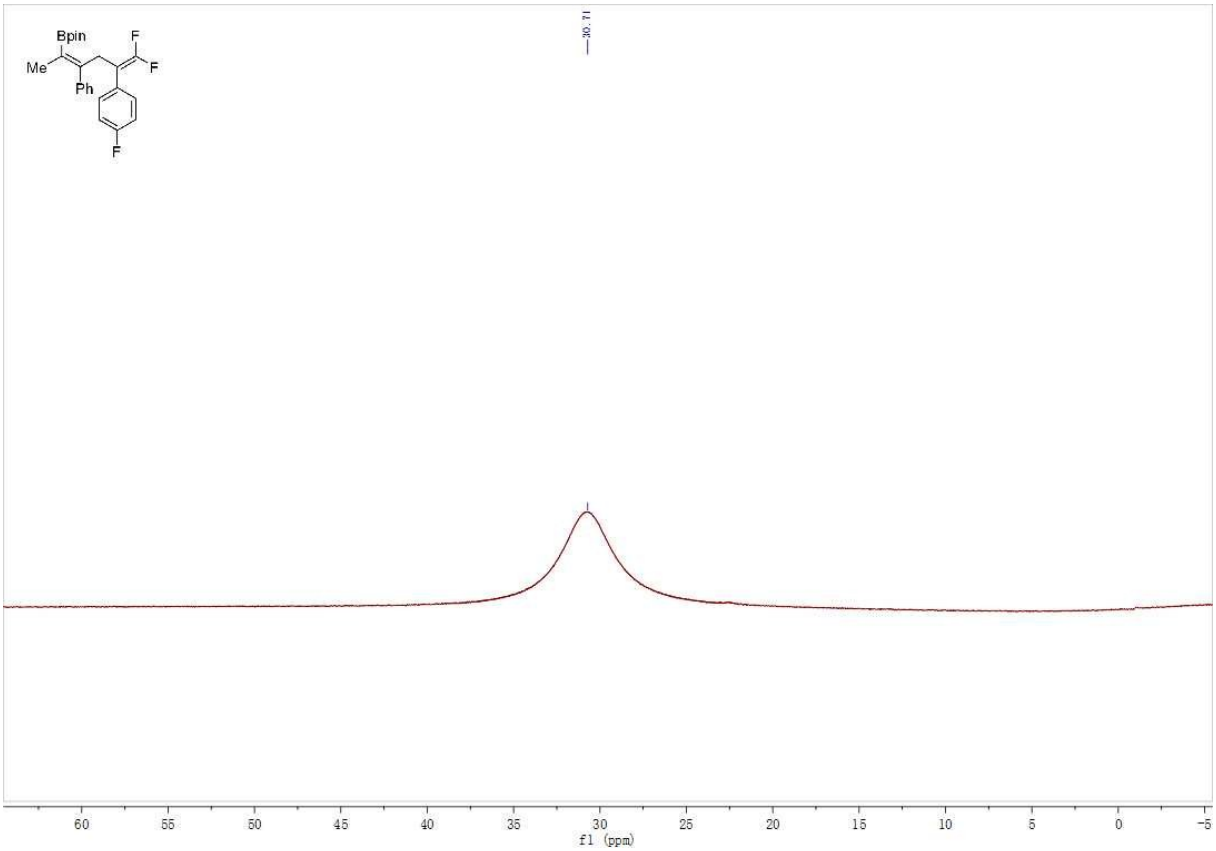


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (56.4 g, 68 %).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.11 (m, 5H), 6.98 – 6.89 (m, 2H), 6.84 (d, *J* = 6.9 Hz, 2H), 3.90 (s, 2H), 1.49 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.70 (d, *J* = 246.1 Hz), 153.89 (dd, *J* = 290.0, 287.6 Hz), 151.87, 141.62, 130.46, 129.45, 127.93, 127.76, 126.59, 116.44, 114.78 (d, *J* = 21.4 Hz), 90.31 (dd, *J* = 21.5, 13.2 Hz), 83.27, 34.49, 24.91, 18.62. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.34 (d, *J* = 41.3 Hz), -92.46 (d, *J* = 41.3 Hz), -115.30. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.71. HRMS (ESI^{+}): Calcd for $C_{24}H_{26}BF_3O_2$ [H]$^{+}$: 415.2056, Found: 415.2066.

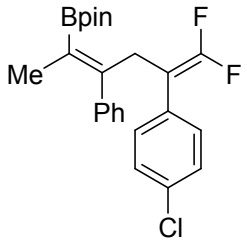



Bpin
F
Me
F
Ph
F
162.93
160.47
156.75
153.90
153.88
151.85
151.01
141.62
130.60
130.57
130.53
130.49
130.46
127.76
114.89
114.68
90.48
90.35
90.27
90.14
83.27
34.49
24.91
18.62
f1 (ppm)

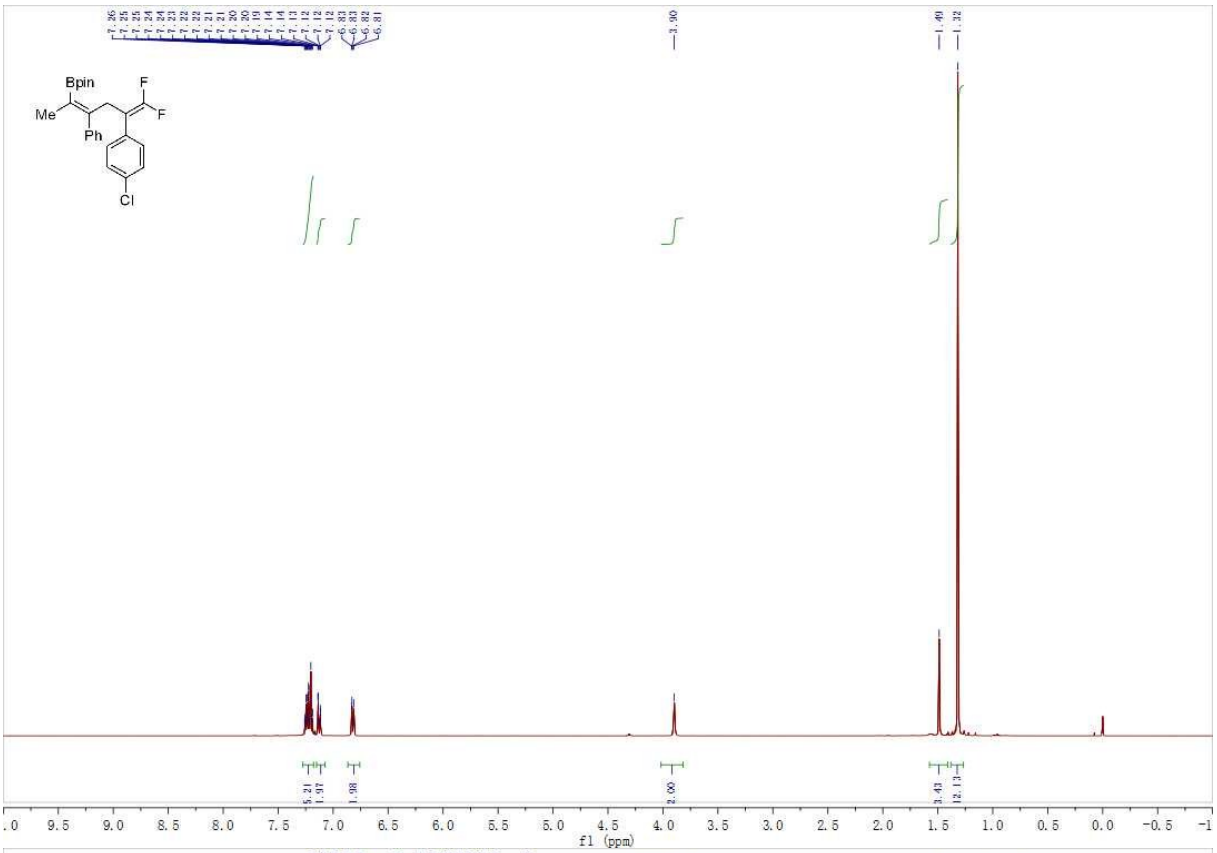

Bpin
F
Me
F
Ph
F
91.28
91.39
92.41
92.52
115.30
f1 (ppm)

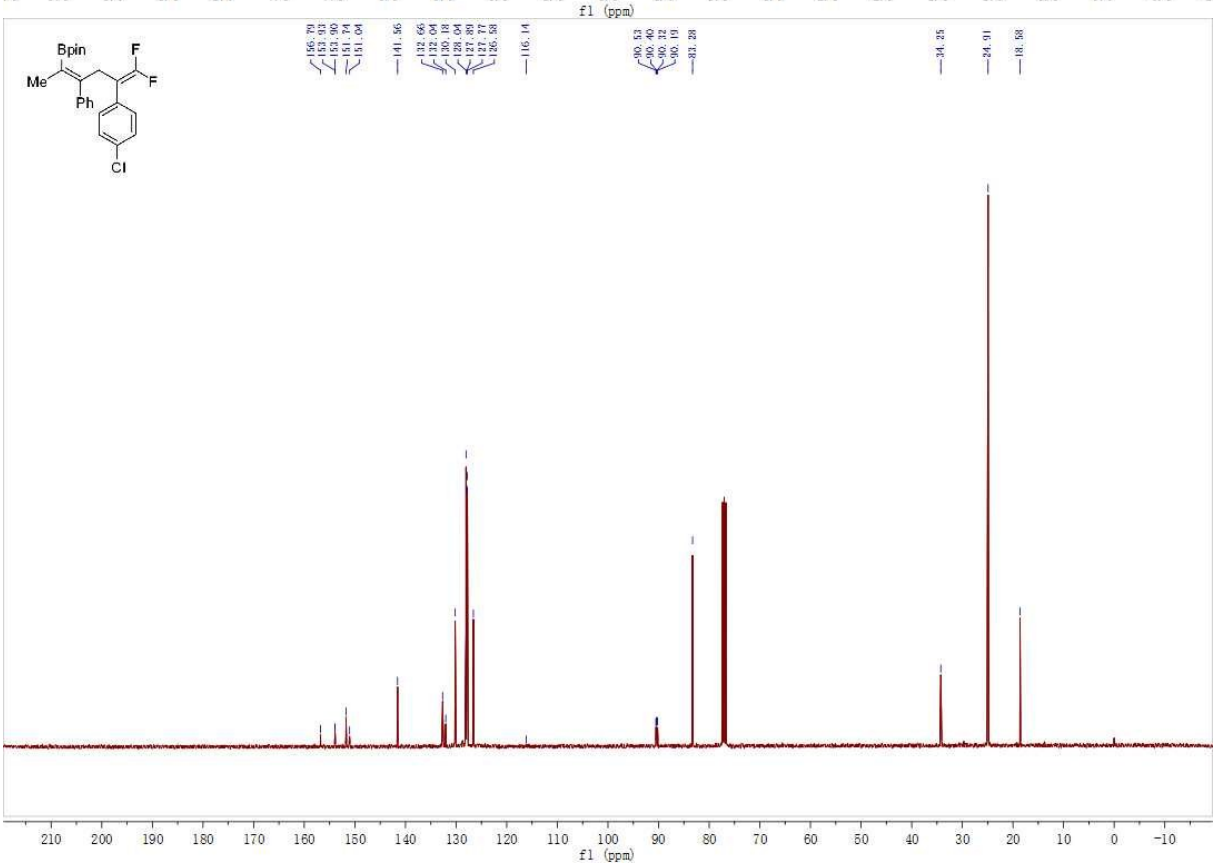


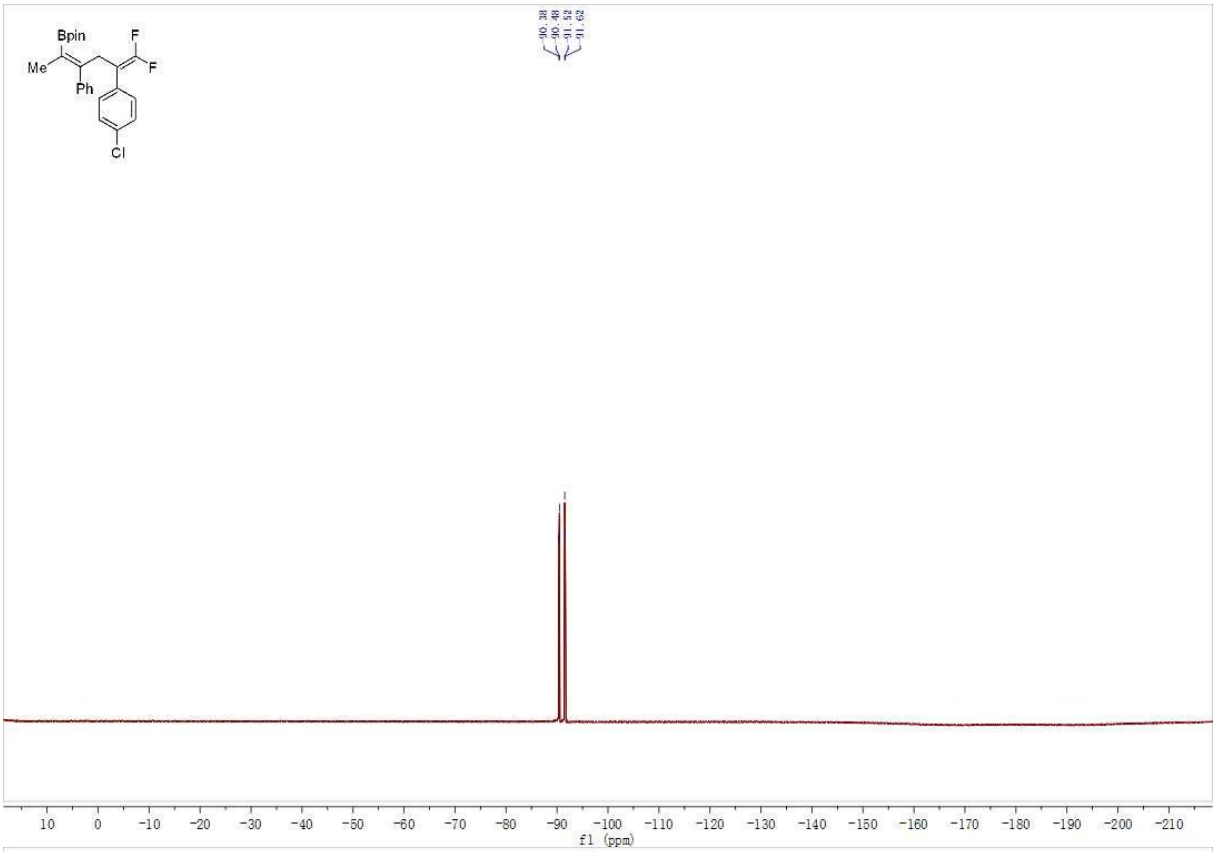
(Z)-2-(5-(4-chlorophenyl)-6,6-difluoro-3-phenylhexa-2,5-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4m)

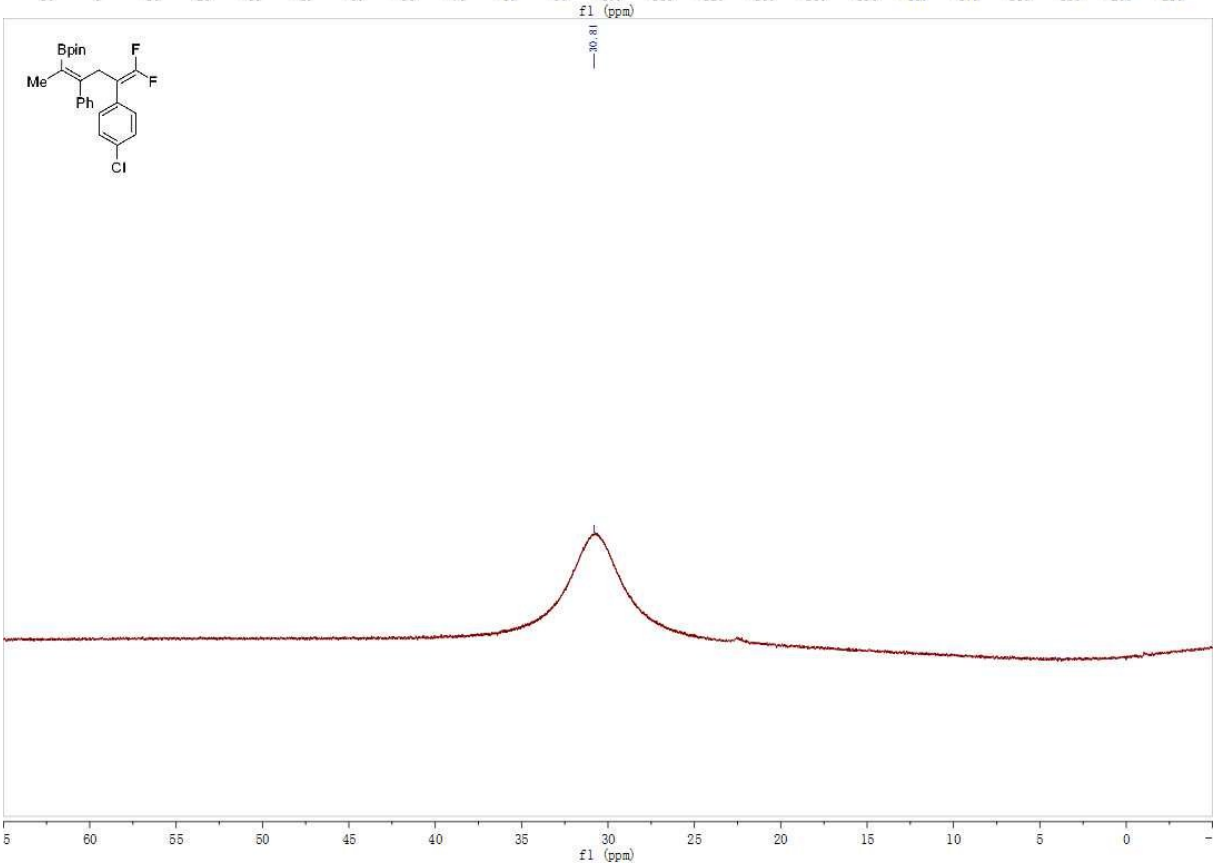


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (51.7 g, 60 %).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.16 (m, 5H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 6.6 Hz, 2H), 3.90 (s, 2H), 1.49 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.91 (dd, *J* = 290.8, 287.7 Hz), 151.74, 141.56, 132.66, 132.04, 130.18, 128.04, 127.89, 127.77, 126.58, 116.14, 90.36 (dd, *J* = 21.5, 12.8 Hz), 83.28, 34.25, 24.91, 18.58. ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.43 (d, *J* = 39.4 Hz), -91.57 (d, *J* = 39.4 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.81. HRMS (ESI^+): Calcd for $C_{24}H_{26}BClF_2O_2$ $[H]^+$: 431.1761, Found: 431.1749.

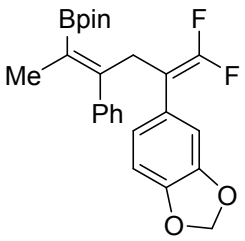

Bpin
F
Me
F
Ph
Cl
f1 (ppm)


Bpin
F
Me
F
Ph
Cl
f1 (ppm)

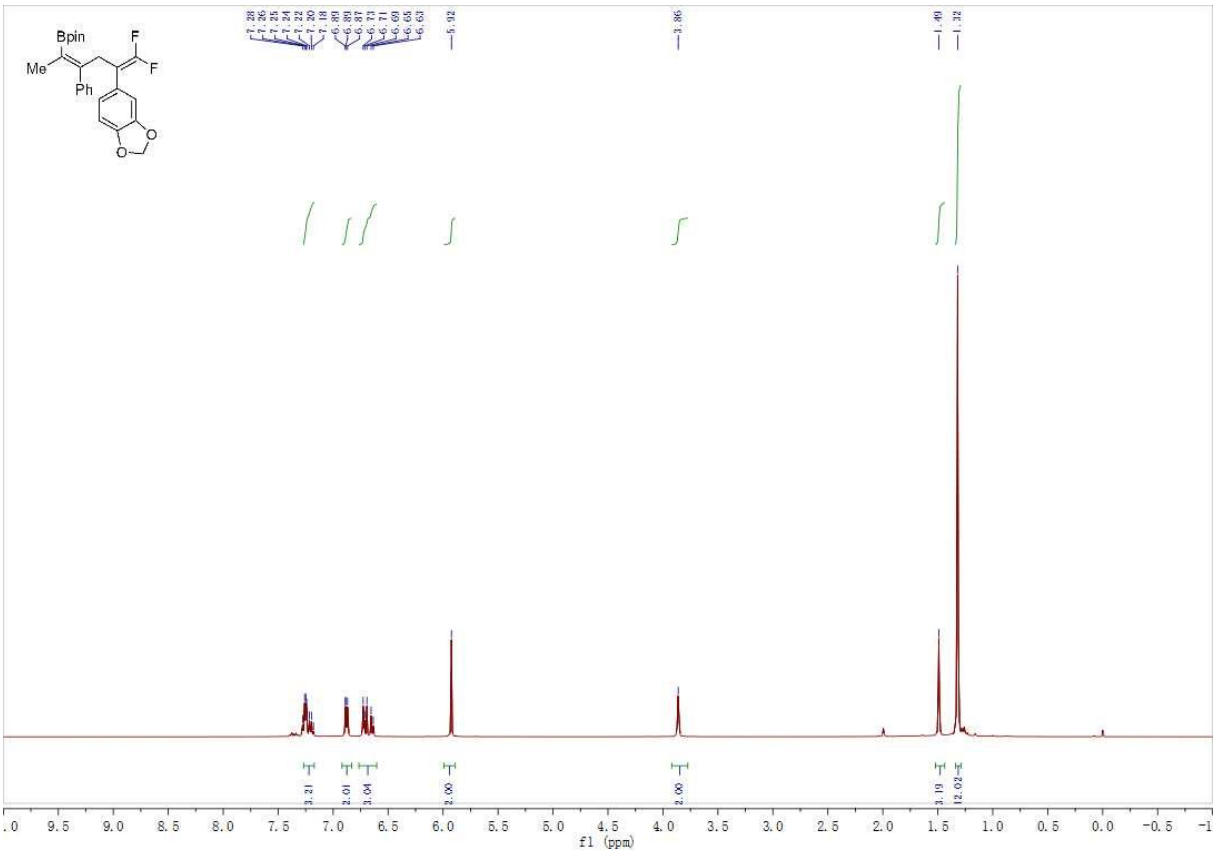

Bpin
F
Me
F
Ph
Cl
-90.38
-90.49
-91.52
-91.62
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

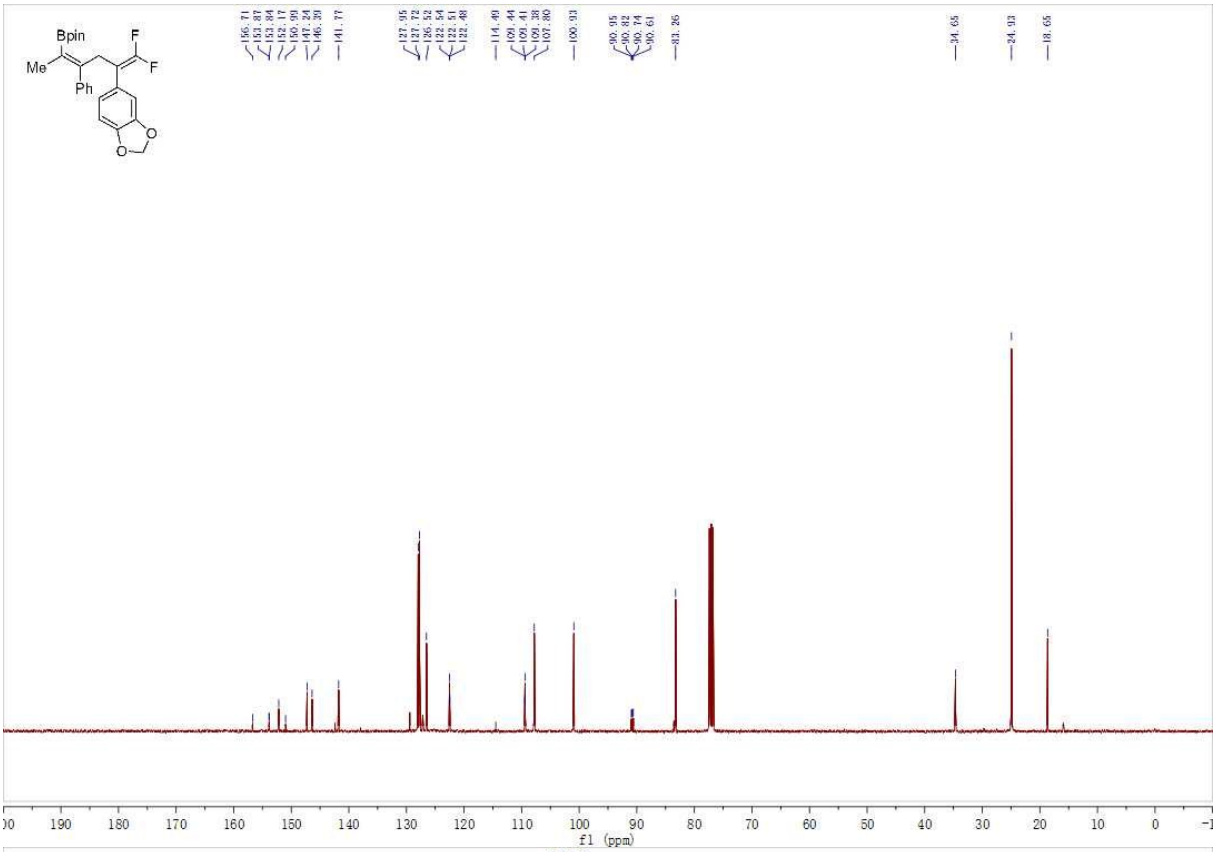

Bpin
F
Me
F
Ph
Cl
30.81
65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

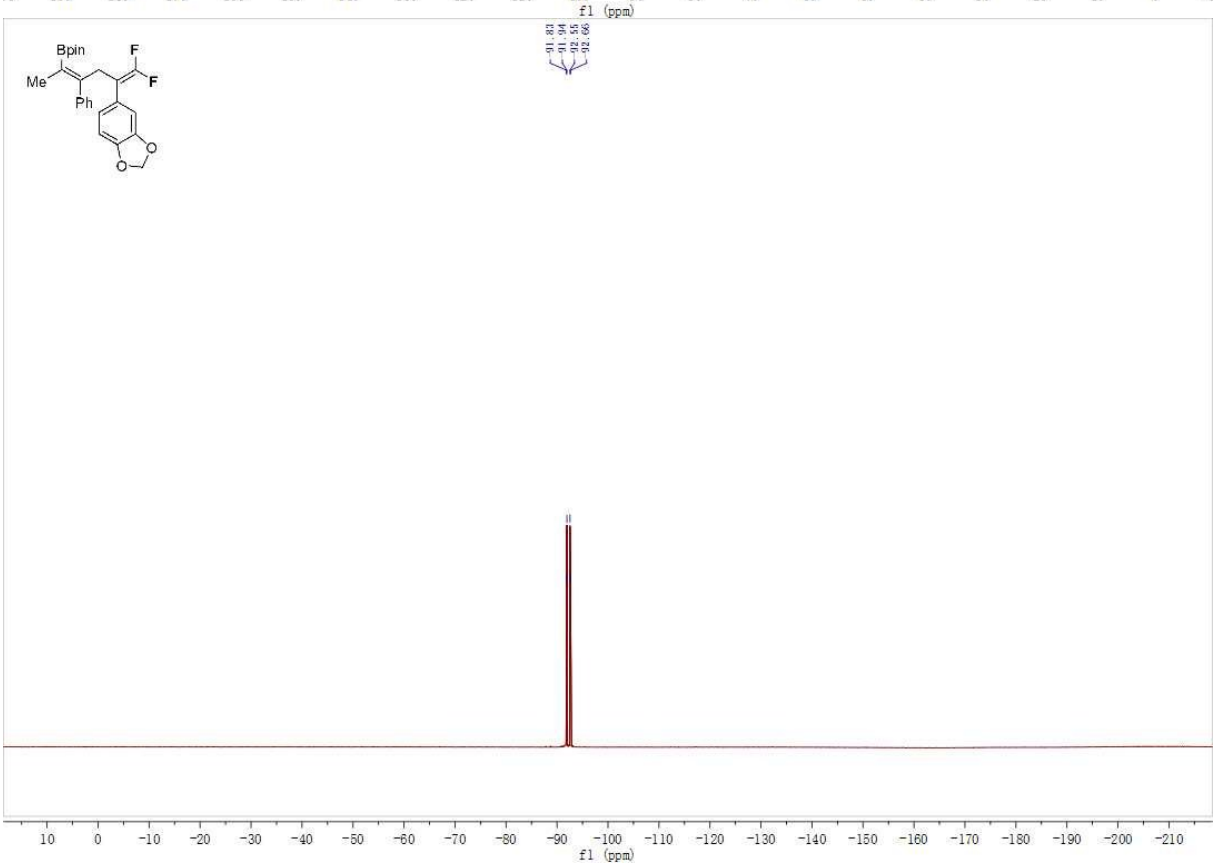
(Z)-2-(5-(benzo[d][1,3]dioxol-5-yl)-6,6-difluoro-3-phenylhexa-2,5-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4n)

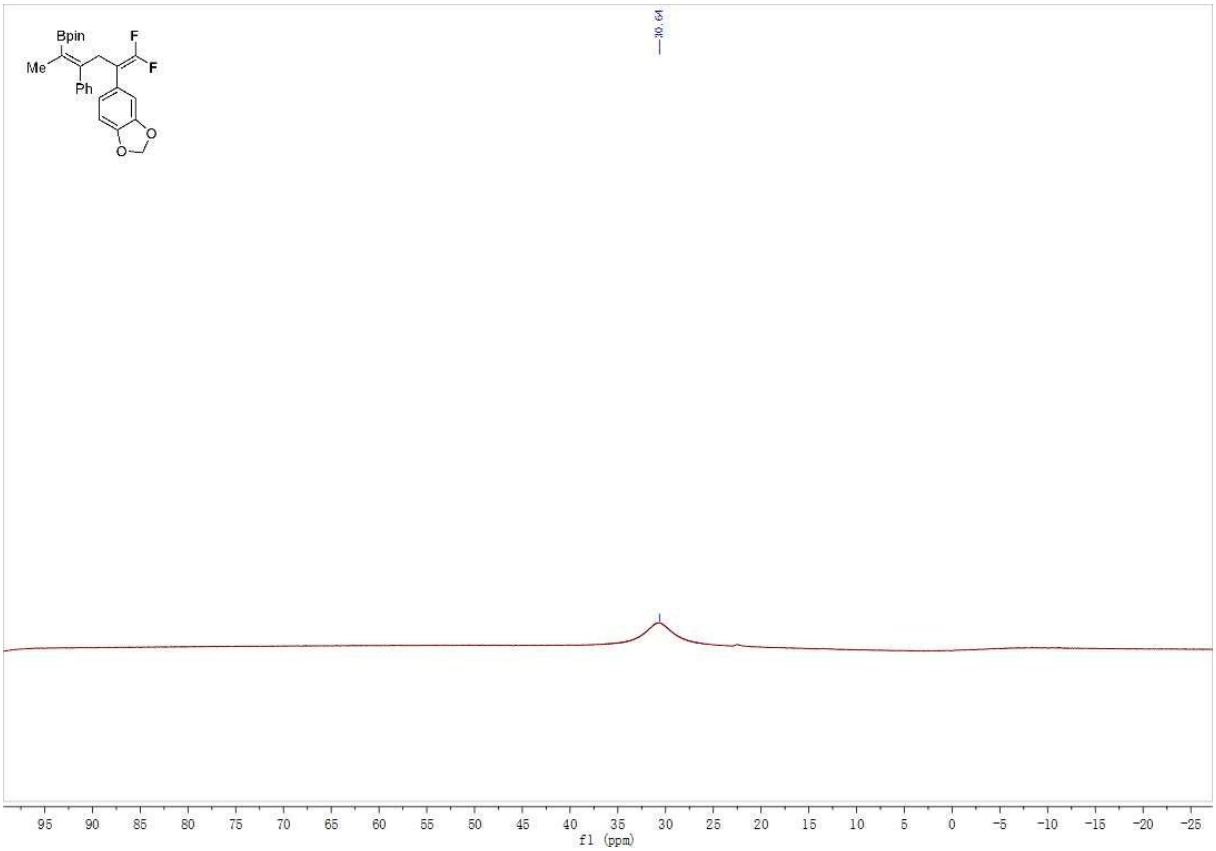


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (30:1) as thick oil (49.4 mg, 56 %).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.14 (m, 3H), 6.99 - 6.83 (m, 2H), 6.76 - 6.62 (m, 3H), 5.92 (s, 2H), 3.86 (s, 2H), 1.49 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.85 (dd, *J* = 289.2, 286.6 Hz), 152.17, 147.24, 146.39, 141.77, 129.43, 127.95, 127.72, 126.52, 122.51, 114.49, 109.41, 107.80, 100.93, 90.78 (dd, *J* = 21.3, 13.2 Hz), 83.26, 34.65, 24.93, 18.65. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.89 (d, *J* = 42.4 Hz), -92.61 (d, *J* = 42.4 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.64. HRMS (ESI^+): Calcd for $C_{25}H_{27}BF_2O_4$ $[H]^+$: 441.2049, Found: 441.2052.

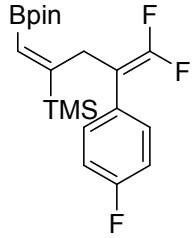



Bpin
F
Me
F
Ph
O
O
156.71
153.87
153.84
152.17
150.99
147.24
146.39
141.77
127.95
127.72
126.52
122.54
122.51
122.48
114.49
109.44
109.41
109.38
107.80
100.93
90.95
90.82
90.74
90.61
83.26
34.65
24.93
18.65
f1 (ppm)

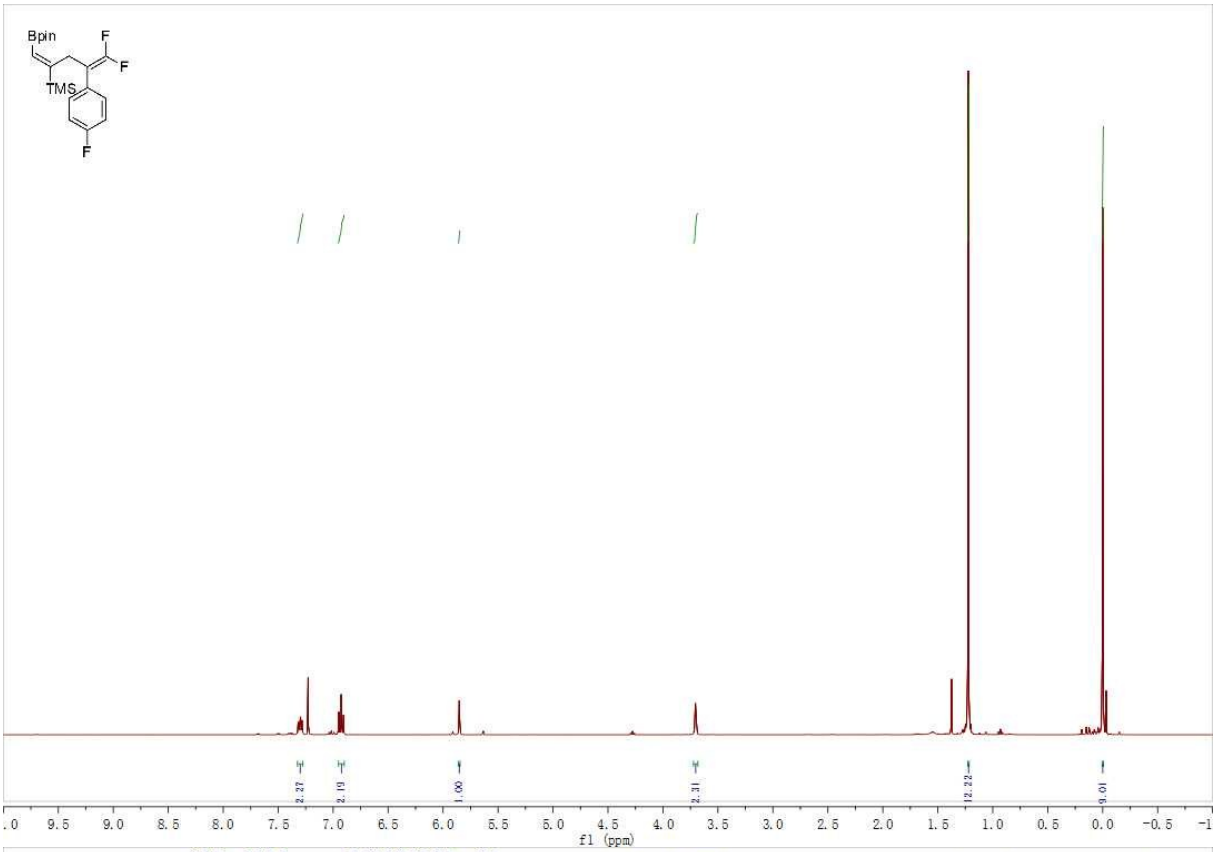

Bpin
F
Me
F
Ph
O
O
91.83
91.94
92.55
92.66
f1 (ppm)

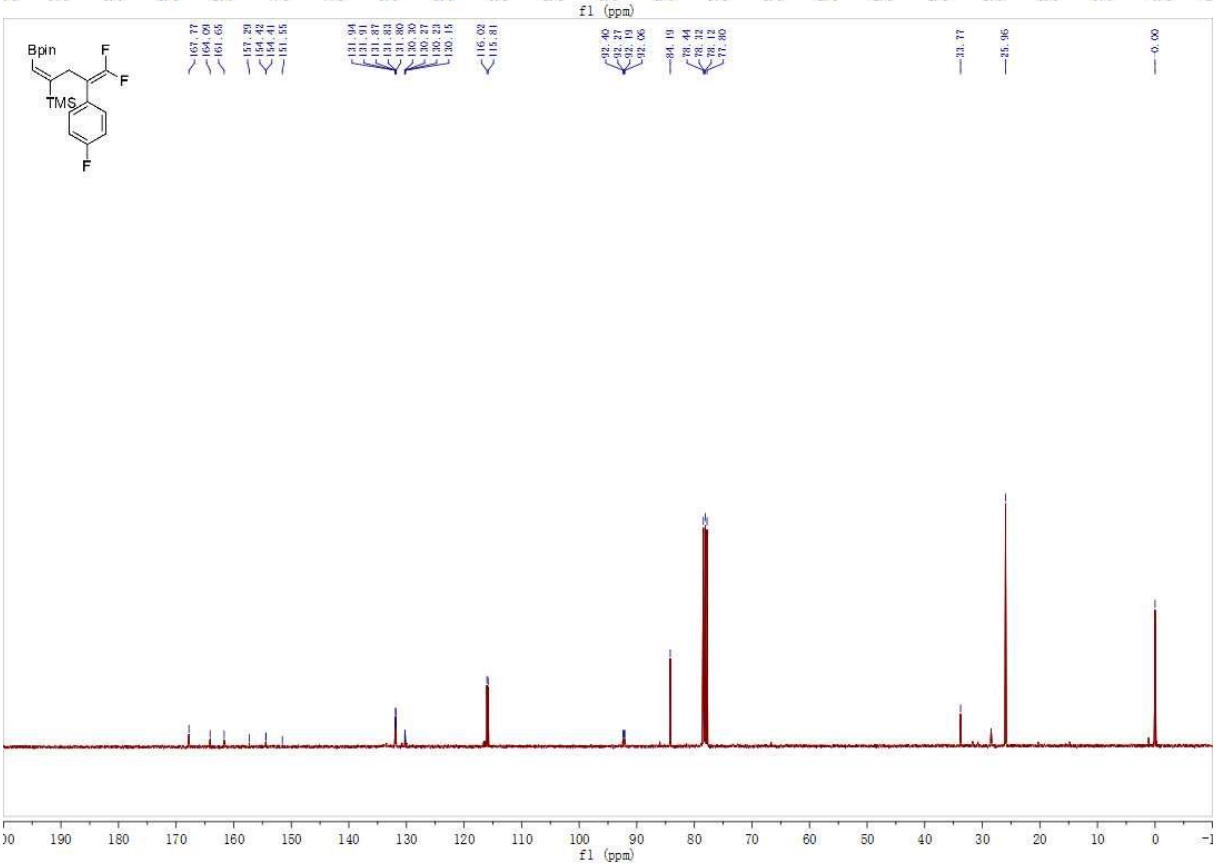


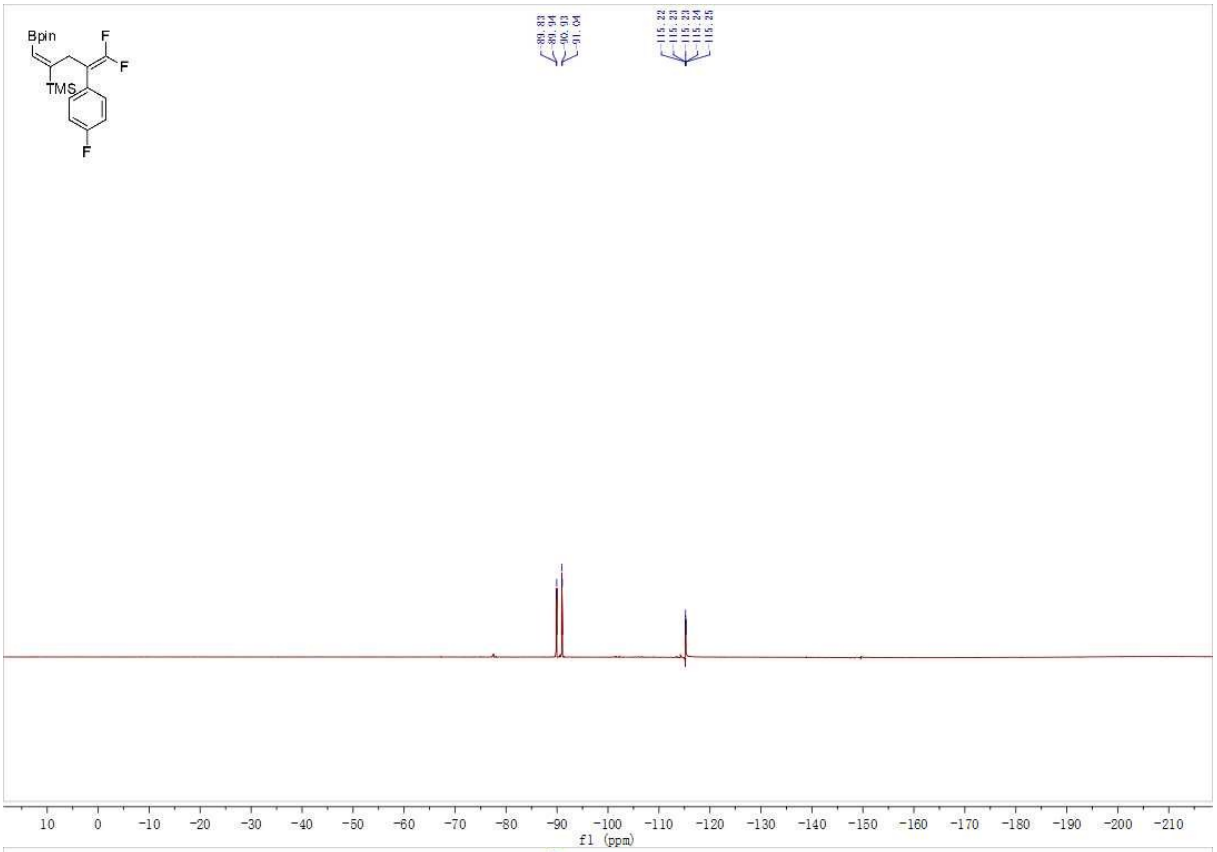
(E)-(5,5-difluoro-4-(4-fluorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)penta-1,4-dien-2-yl)trimethylsilane (4o)

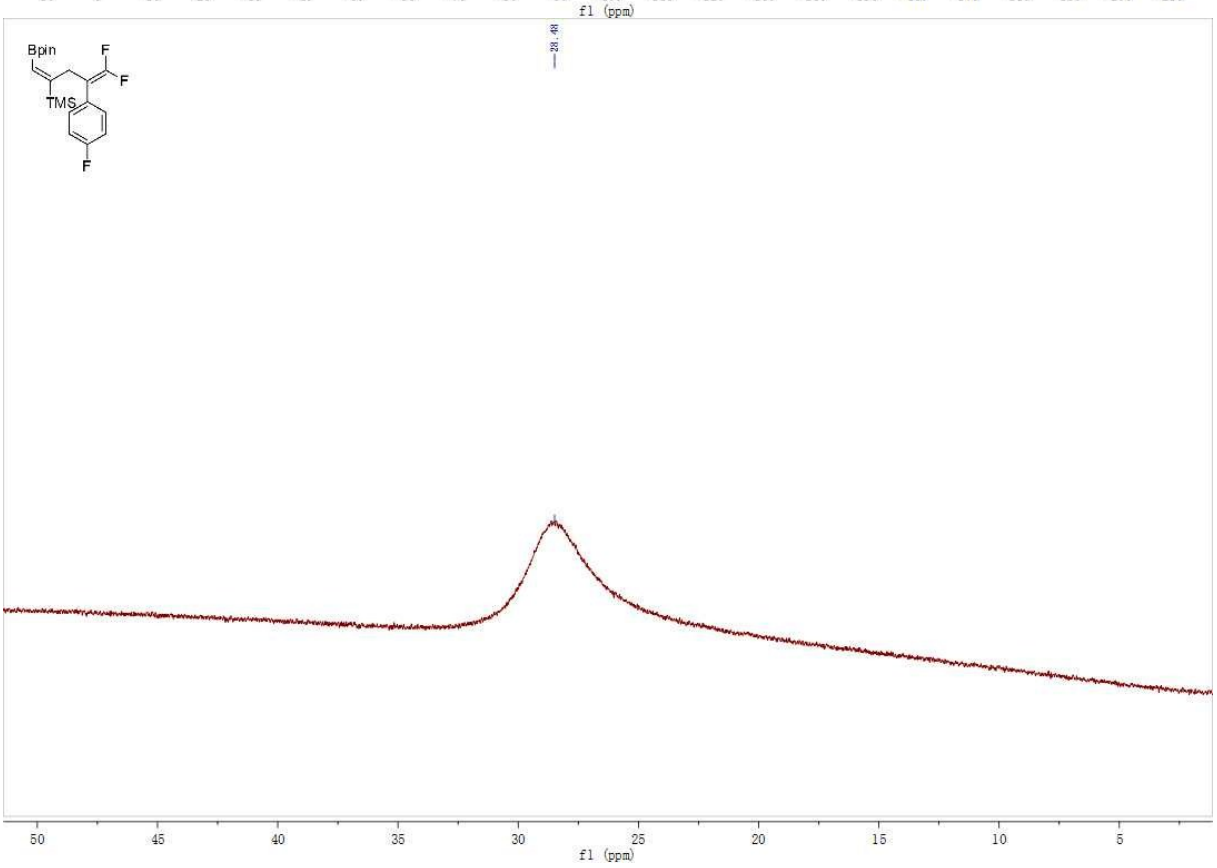


Following general procedure, The product was isolated by column chromatography with hexane/ethyl acetate (100:1) as thick oil (55.6 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.26 (m, 2H), 6.97 - 6.87 (m, 2H), 5.85 (s, 1H), 3.71 (s, 2H), 1.22 (s, 12H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.77, 164.09, 154.42 (dd, *J* = 289.5, 288.0 Hz), 131.87, 130.23, 116.02, 115.81, 92.23 (dd, *J* = 21.1, 12.6 Hz), 84.19, 33.77, 25.96. ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.89 (d, *J* = 41.8 Hz), -90.98 (d, *J* = 41.8 Hz), -115.22 (s). ^{11}B NMR (128 MHz, $CDCl_3$) δ 28.48. HRMS (ESI^+): Calcd for $C_{20}H_{28}BF_3O_2Si$ $[H]^+$: 397.1982, Found: 397.1988.

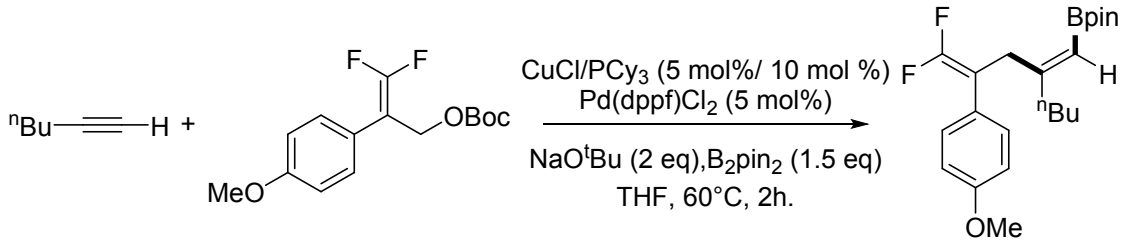

Bpin
F
F
TMS
F
2.27
2.19
1.00
2.31
12.22
9.01
f1 (ppm)


Bpin
F
F
TMS
F
167.17
164.09
161.65
157.29
154.42
154.41
151.55
131.94
131.91
131.87
131.83
131.80
130.30
130.27
130.23
130.15
116.02
115.81
92.40
92.27
92.19
92.06
84.19
78.44
78.12
77.80
33.77
25.95
0.00
f1 (ppm)

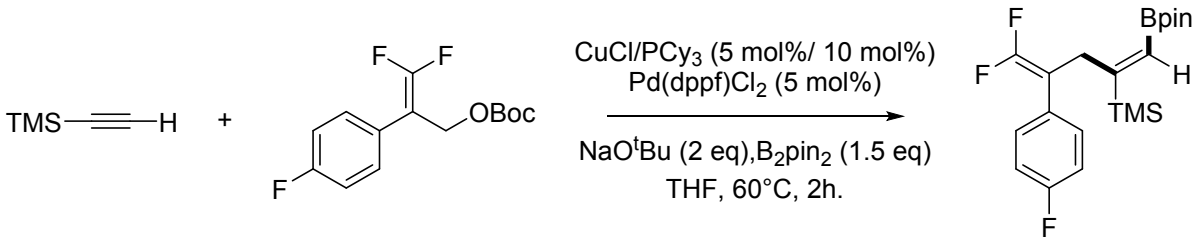

Bpin
F
F
TMS
F
-89.83
-89.94
-90.93
-91.04
-115.22
-115.23
-115.24
-115.25
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


Bpin
F
F
TMS
F
28.48
50 45 40 35 30 25 20 15 10 5
f1 (ppm)

3.3 Gram-scale reaction



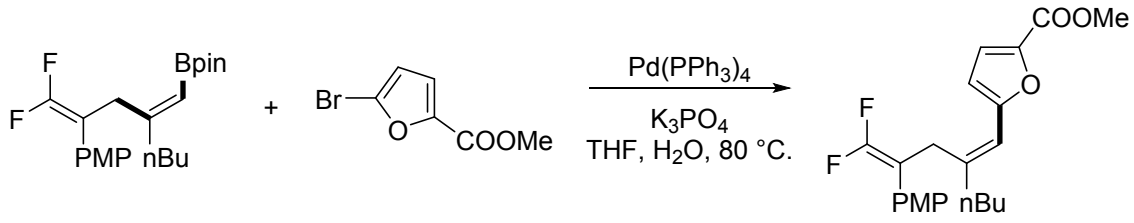
In an Ar-filled dry box, CuCl (5 mol%, 49.5 mg) and PCy_3 (10 mol%, 280.4 mg) were added to a 100 mL Schlenk tube containing a magnetic stirring bar. Then the dry THF (30 mL) were added to the mixture, The Schlenk tube was sealed and removed from the dry box and stirred during 15 minutes at r.t. Then B_2pin_2 (1.5 eq, 15 mmol, 3.8 g) and NaO^tBu (2.0 equiv, 20 mmol, 1.9 g) were added to the mixture to afford a black suspension. In a separate vial $Pd(dppf)Cl_2$ (5 mol%, 365.8 mg) and tert-butyl (3,3-difluoro-2-(4-methoxyphenyl)allyl) carbonate (1.5 equiv, 15 mmol, 4.5 g) were stirred in dry THF (5 mL) for 15 minutes at r.t. The hex-1-yne (1 equiv, 10 mmol, 0.8 g) and This solution and was finally added to the Schlenk tube and heated at 60 ºC for 2h. After this time, then reaction was cooled to room temperature. Et_2O and water were added and the layers were separated. The aqueous phase was extracted with Et_2O (x 2) and the combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel to give **3a** (3.1 g, 78 %).



In an Ar-filled dry box, CuCl (5 mol%, 24.7 mg) and PCy_3 (10 mol%, 140 mg) were added to a 100 mL Schlenk tube containing a magnetic stirring bar. Then the dry THF (30 mL) were added to the mixture, The Schlenk tube was

sealed and removed from the dry box and stirred during 15 minutes at r.t. Then B_2pin_2 (1.5 eq, 7.5 mmol, 1.9 g) and NaO^tBu (2.0 equiv, 10 mmol, 0.96 g) were added to the mixture to afford a black suspension. In a separate vial $Pd(dppf)Cl_2$ (5 mol%, 183 mg) and tert-butyl (3,3-difluoro-2-(4-fluorophenyl)allyl) carbonate (1.5 equiv, 7.5 mmol, 2.2 g) were stirred in dry THF (5 mL) for 15 minutes at r.t. The ethynyltrimethylsilane (1 eq, 5 mmol, 490 mg) and This solution and was finally added to the Schlenk tube and heated at 60 ºC for 2h. After this time, then reaction was cooled to room temperature. Et_2O and water were added and the layers were separated. The aqueous phase was extracted with Et_2O (x 2) and the combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel to give **4o** (1.4 g, 70 %).

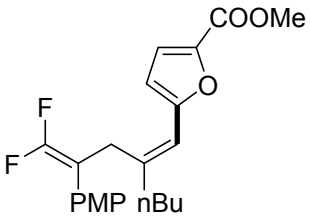
3.4 Experimental Procedures for example described in application:



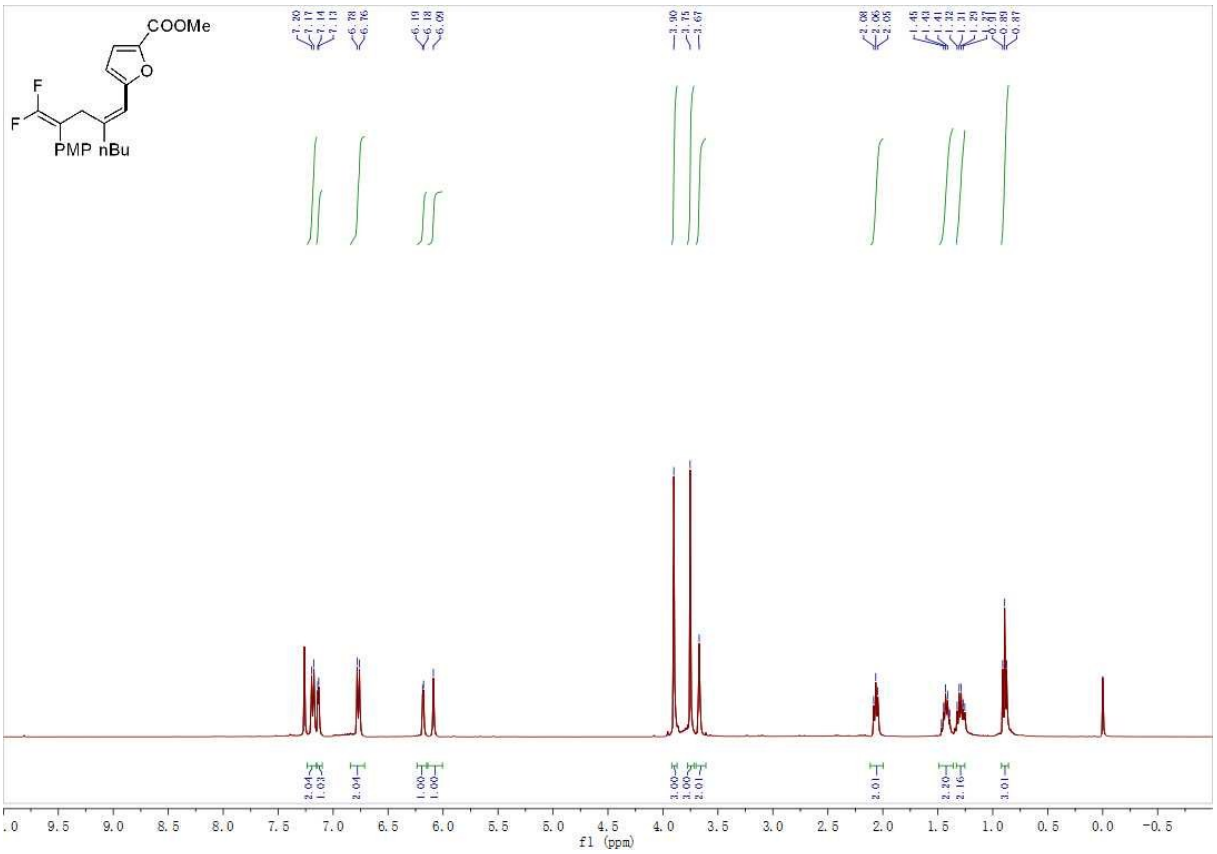
3a **5**

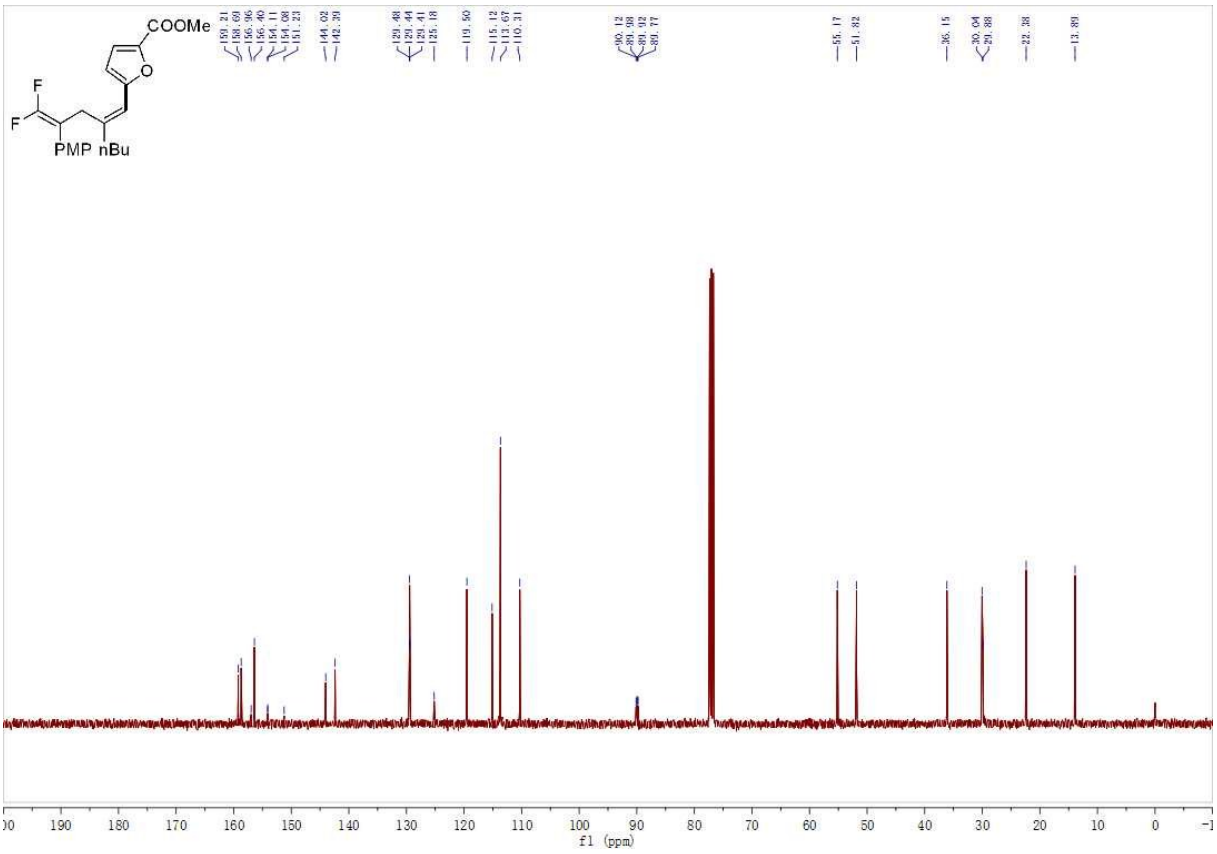
To the **3a** (0.3 mmol, 117.6 mg, 1.5 eq) product in $Pd(PPh_3)_4$ (11.55 mg, 0.05 eq), K_3PO_4 (0.6 mmol, 127.2 mg, 3 eq), THF (2 mL) and H_2O (1 mL) was added methyl 5-bromofuran-2-carboxylate (0.2 mmol, 40.78 mg, 1 eq), the resulting mixture was stirred at 80 ℃ for 8 h. The resulting mixture was quenched with brine. The mixture was extracted with ethyl acetate and the combined organic layer was dried over Na_2SO_4. Then the orgnic layer was concentrated and the residue was purified by columnchromatography with hexane/ethyl acetate (30:1) to give **5** as a thick oil (70.2 mg, 90 %).

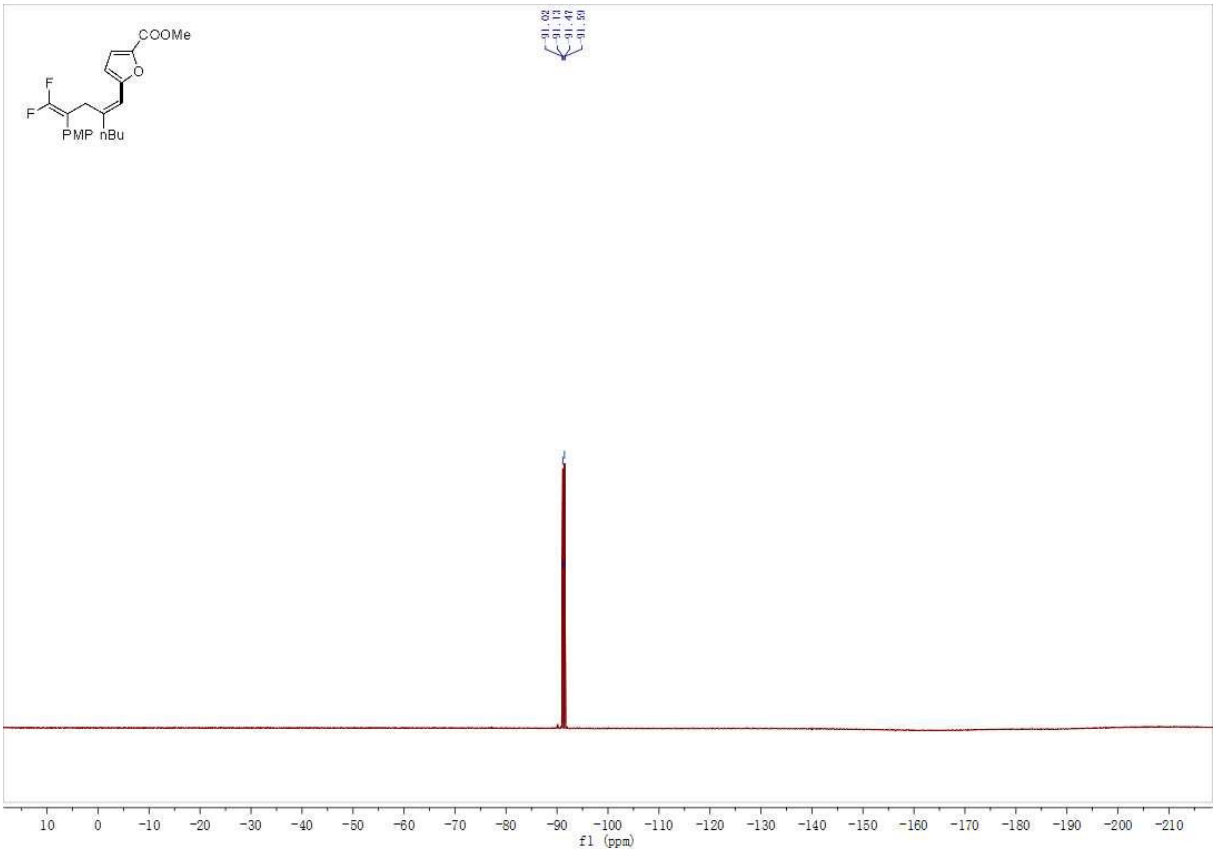
methyl (Z)-5-(2-(3,3-difluoro-2-(4-methoxyphenyl)allyl)hex-1-en-1-yl)furan-2-carboxylate (5)

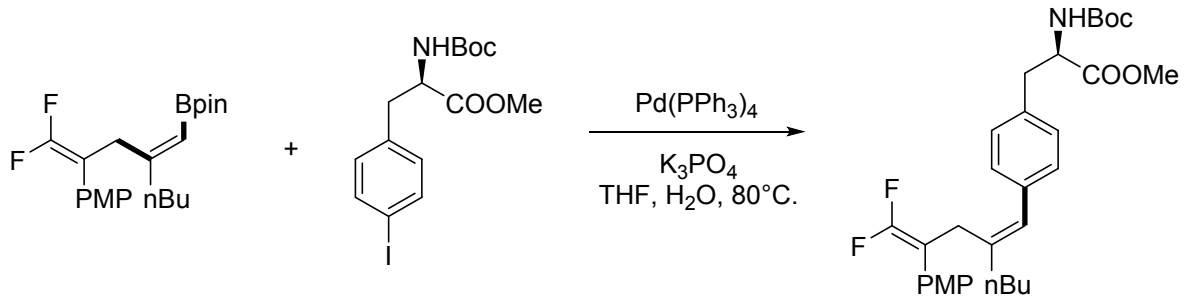


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 3.5 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.18 (d, *J* = 3.4 Hz, 1H), 6.09 (s, 1H), 3.90 (s, 3H), 3.75 (s, 3H), 3.67 (s, 2H), 2.06 (t, *J* = 7.6 Hz, 2H), 1.48 - 1.38 (m, 2H), 1.33 - 1.25 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.21, 158.69, 156.40, 154.10 (dd, *J* = 289.8, 286.9 Hz), 144.02, 142.39, 129.44, 125.18, 119.50, 115.12, 113.67, 110.31, 89.95 (dd, *J* = 20.8, 14.4 Hz), 55.17, 51.82, 36.15, 30.04, 29.88, 22.38, 13.89. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.08 (d, *J* = 43.4 Hz), -91.53 (d, *J* = 43.4 Hz). HRMS (ESI^+): Calcd for $C_{22}H_{24}F_2O_4$ $[H]^+$: 391.1721, Found: 391.1721.




COOMe
F
F
PMP nBu
159.21
158.69
156.96
156.40
154.11
154.08
151.23
144.02
142.39
129.48
129.44
129.41
125.18
119.50
115.12
113.67
110.31
90.12
89.98
89.92
89.77
55.17
51.82
35.15
30.04
29.88
22.38
13.89
f1 (ppm)

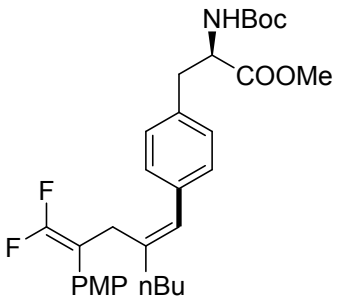

COOMe
F
F
PMP nBu
-91.02
-91.12
-91.47
-91.59
f1 (ppm)



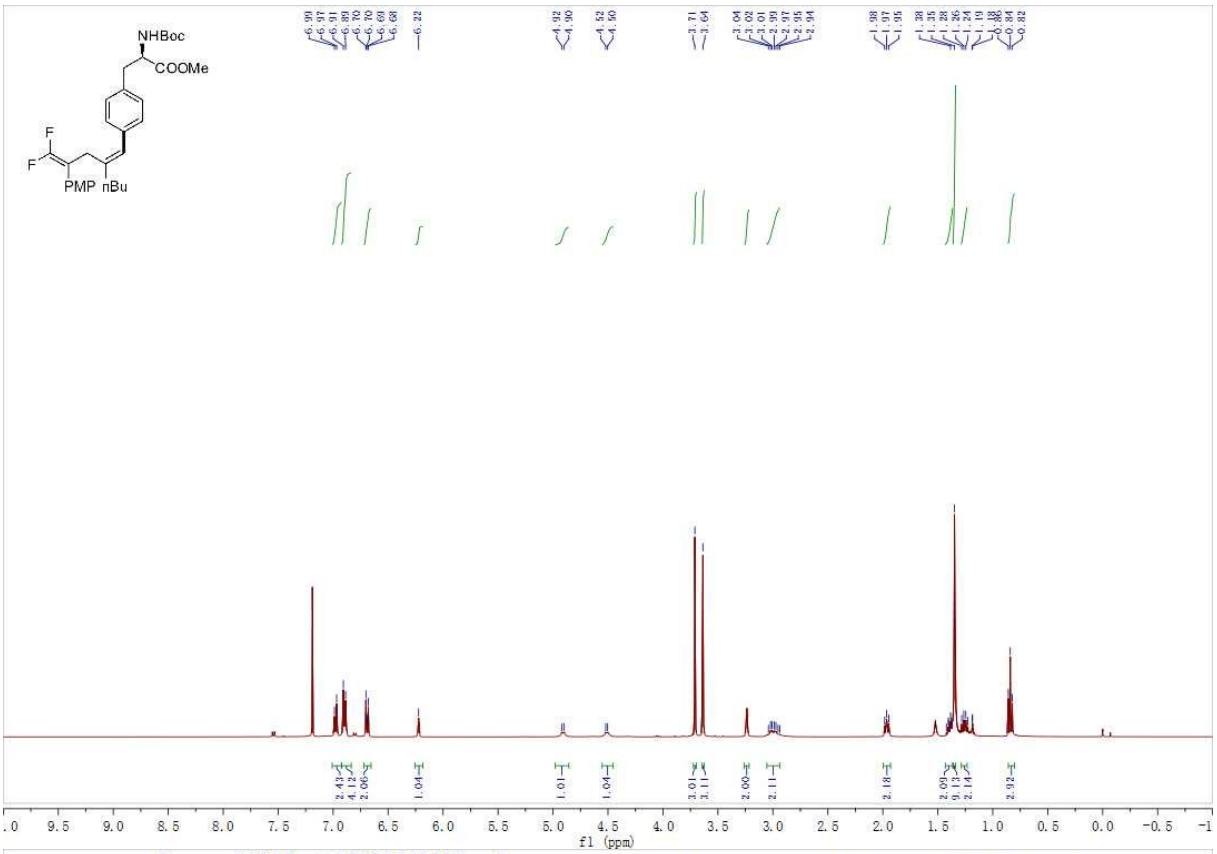
3a **6**

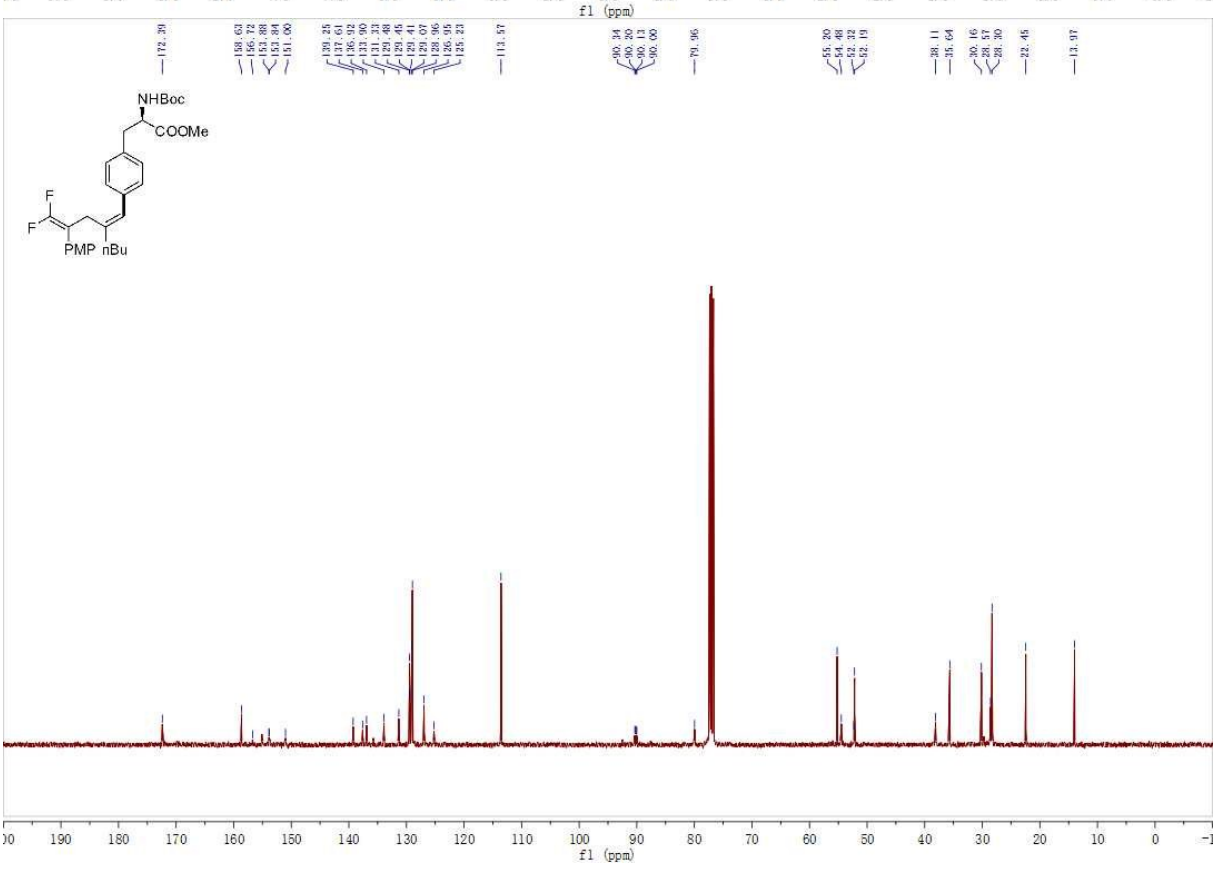
To the **3a** (0.3 mmol, 117.6 mg, 1.5 eq) product in $Pd(PPh_3)_4$ (11.55 mg, 0.05 eq), K_3PO_4 (0.6 mmol, 127.2 mg, 3 eq), THF (2 mL) and H_2O (1 mL) was added methyl methyl 2-((tert-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate (0.2 mmol, 81 mg, 1 eq), the resulting mixture was stirred at 80 ℃ for 8 h.The resulting mixture was quenched with brine. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over Na_2SO_4. Then the orgnic layer was concentrated and the residue was purified by columnchromatography with hexane/ethyl acetate (5:1) to give the **6** as a white solid (81.5 mg, 75%).

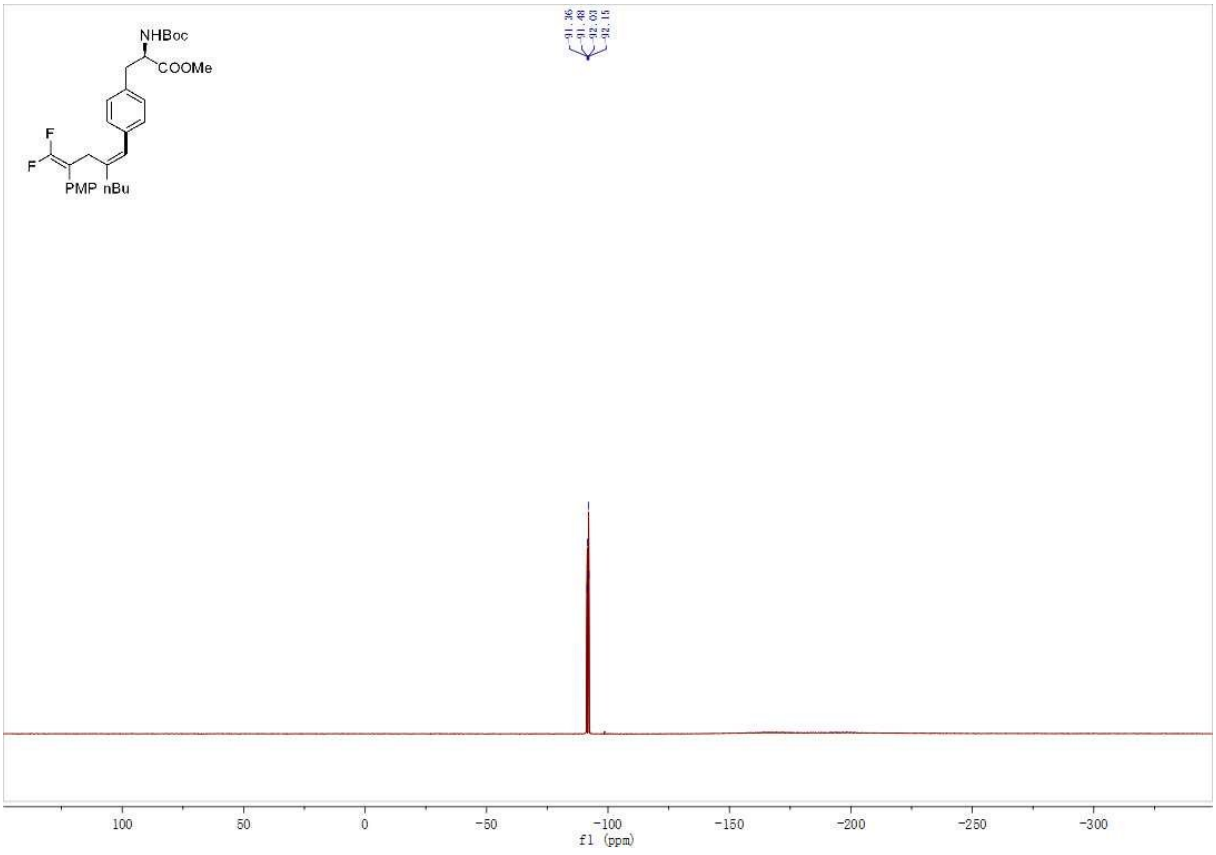
Methyl (Z)-2-((tert-butoxycarbonyl)amino)-3-(4-(2-(3,3-difluoro-2-(4-methoxyphenyl)allyl)hex-1-en-1-yl)phenyl)propanoate (6)

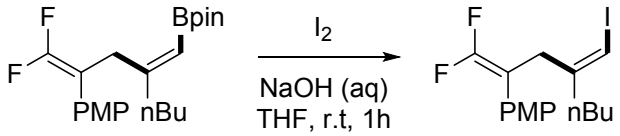


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 4H), 6.75 - 6.60 (m, 2H), 6.22 (s, 1H), 4.91 (d, *J* = 7.6 Hz, 1H), 4.62 – 4.55 (q, 1H), 3.71 (s, 3H), 3.64 (s, 3H), 3.24 (s, 2H), 3.07 - 2.86 (m, 2H), 1.96 (t, *J* = 7.3 Hz, 2H), 1.45 - 1.37 (m, 2H), 1.35 (s, 9H), 1.31 - 1.11 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 158.63, 153.86 (dd, *J* = 289.7, 286.3 Hz), 139.25, 137.61, 136.92, 133.90, 131.33, 129.45, 129.07, 128.96, 126.95, 125.23, 113.57, 90.17 (dd, *J* = 20.7, 13.5 Hz), 79.96, 55.20, 54.48, 52.19, 38.11, 35.64, 30.16, 28.57, 28.30, 22.45, 13.97. ^{19}F NMR (377 MHz, $CDCl_3$) δ -91.42 (d, *J* = 44.5 Hz), -92.09 (d, *J* = 44.5 Hz). HRMS (ESI^+): Calcd for $C_{31}H_{39}F_2NO_5$ $[Na]^+$: 544.2875, Found: 544.2872.


NHBoc
COOMe
F
F
PMP nBu
f1 (ppm)


NHBoc
COOMe
F
F
PMP nBu
f1 (ppm)

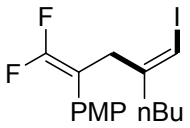




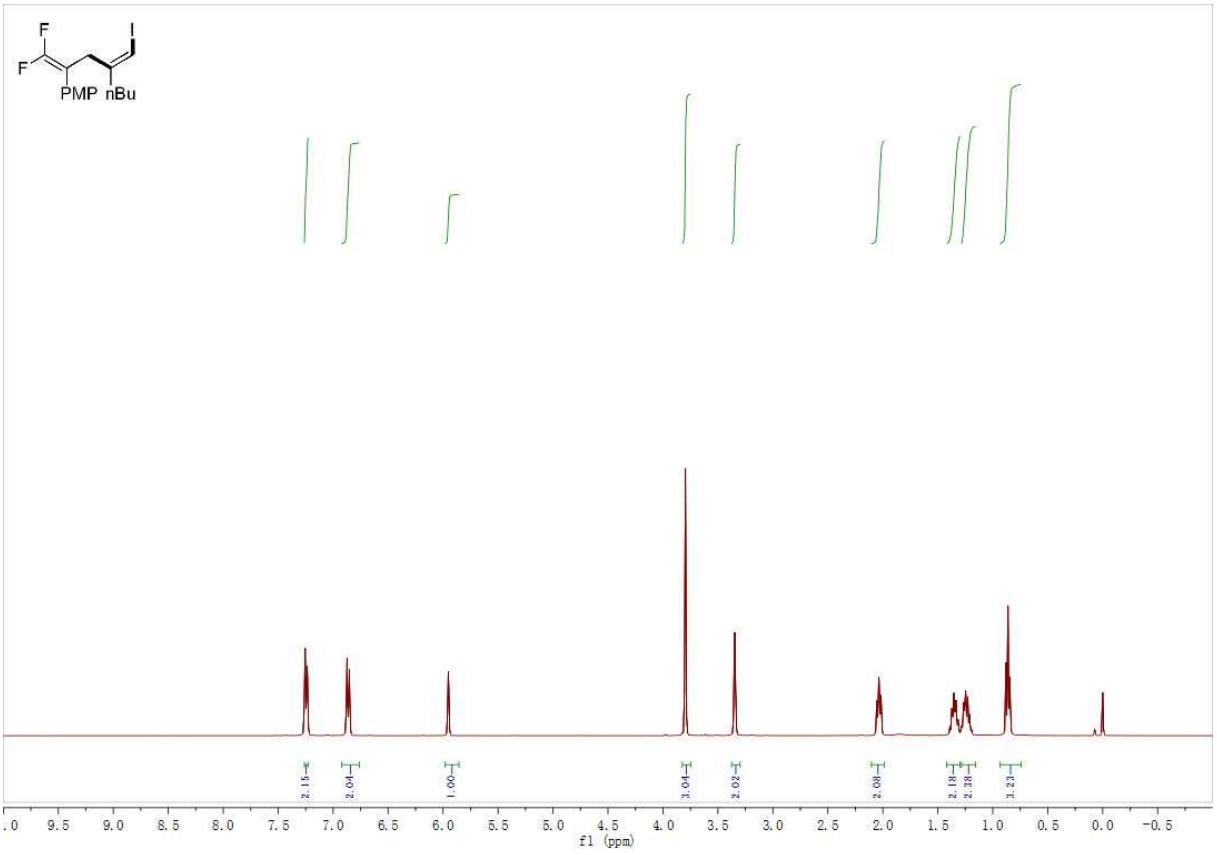
3a **7**

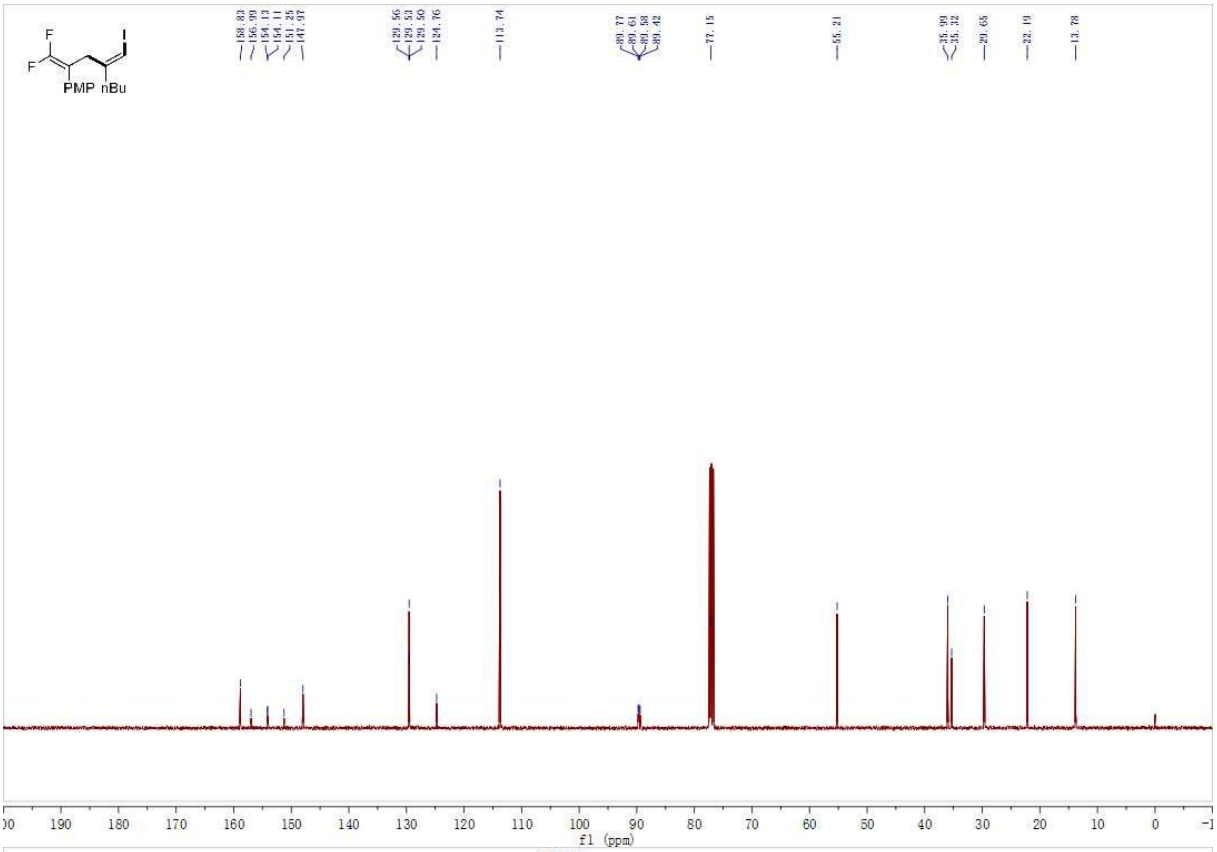
To a solution of **3a** (0.2 mmol, 78.4 mg, 1 eq) in THF (1 mL) were added a solution of NaOH (0.1 mL, 0.3 mmol, 3 M in water). The obtained mixture was stirred for 10 min at 23 °C, followed by dropwise addition of a solution of I_2 (50 mg, 0.2 mmol, 1 eq) in THF (1 mL). After 1 h at 23 °C, the reaction mixture was quenched with brine and extracted with ethyl acetate. The combined organic fraction was washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography with hexane to give the **7** as a thick oil (66.6 mg, 85%).

(Z)-1-(1,1-difluoro-4-(iodomethylene)oct-1-en-2-yl)-4-methoxybenzene (7)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.4 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.95 (s, 1H), 3.80 (s, 3H), 3.35 (s, 2H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.42 - 1.30 (m, 2H), 1.28 - 1.18 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.83, 154.12 (dd, *J* = 289.5, 288.2 Hz), 147.97, 129.53, 124.76, 113.74, 89.60 (dd, *J* = 19.2, 16.2 Hz), 77.15, 55.21, 35.99, 35.32, 29.65, 22.19, 13.78. ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.79 (d, *J* = 42.5 Hz), -90.92 (d, *J* = 42.5 Hz). HRMS (ESI^+): Calcd for $C_{16}H_{19}F_3IO$ $[H]^+$: 393.0527, Found: 393.0510.




F
F
I
PMP nBu
158.83
156.99
154.13
154.11
151.35
147.97
129.56
129.53
129.50
124.76
113.74
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89.61
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55.21
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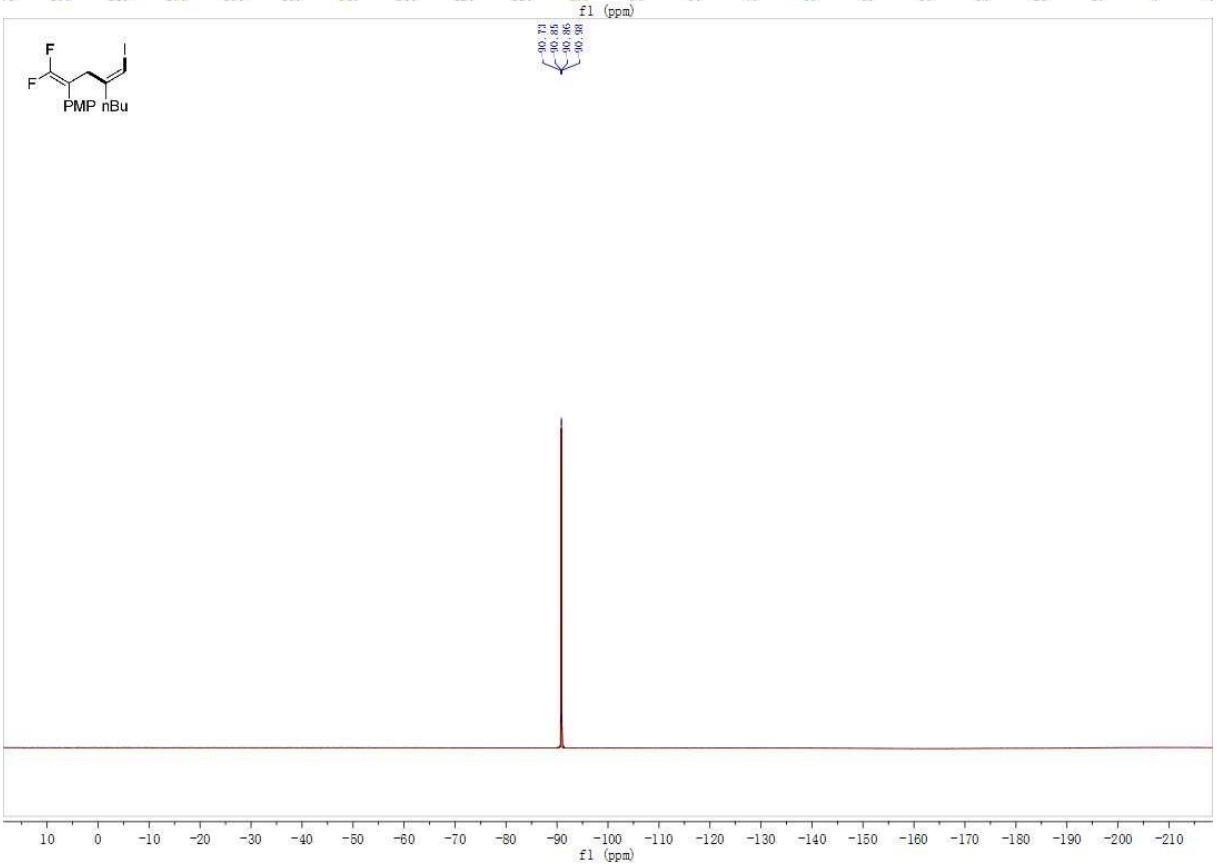
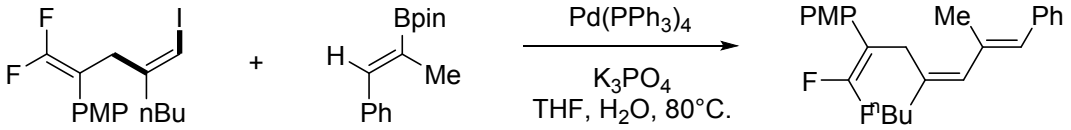
35.32
29.65
22.19
13.78
f1 (ppm)

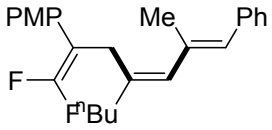

F
F
I
PMP nBu
90.73
90.85
90.86
90.98
f1 (ppm)



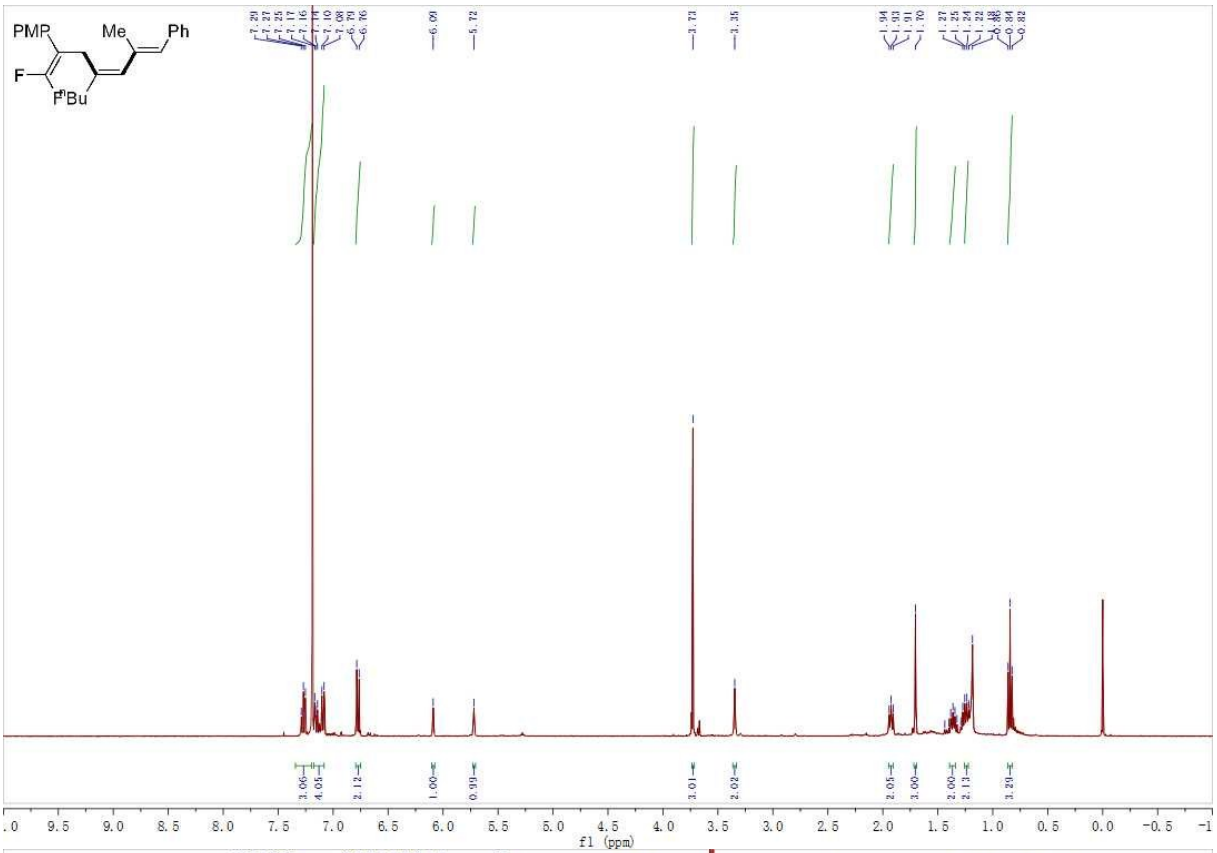
7 **8**

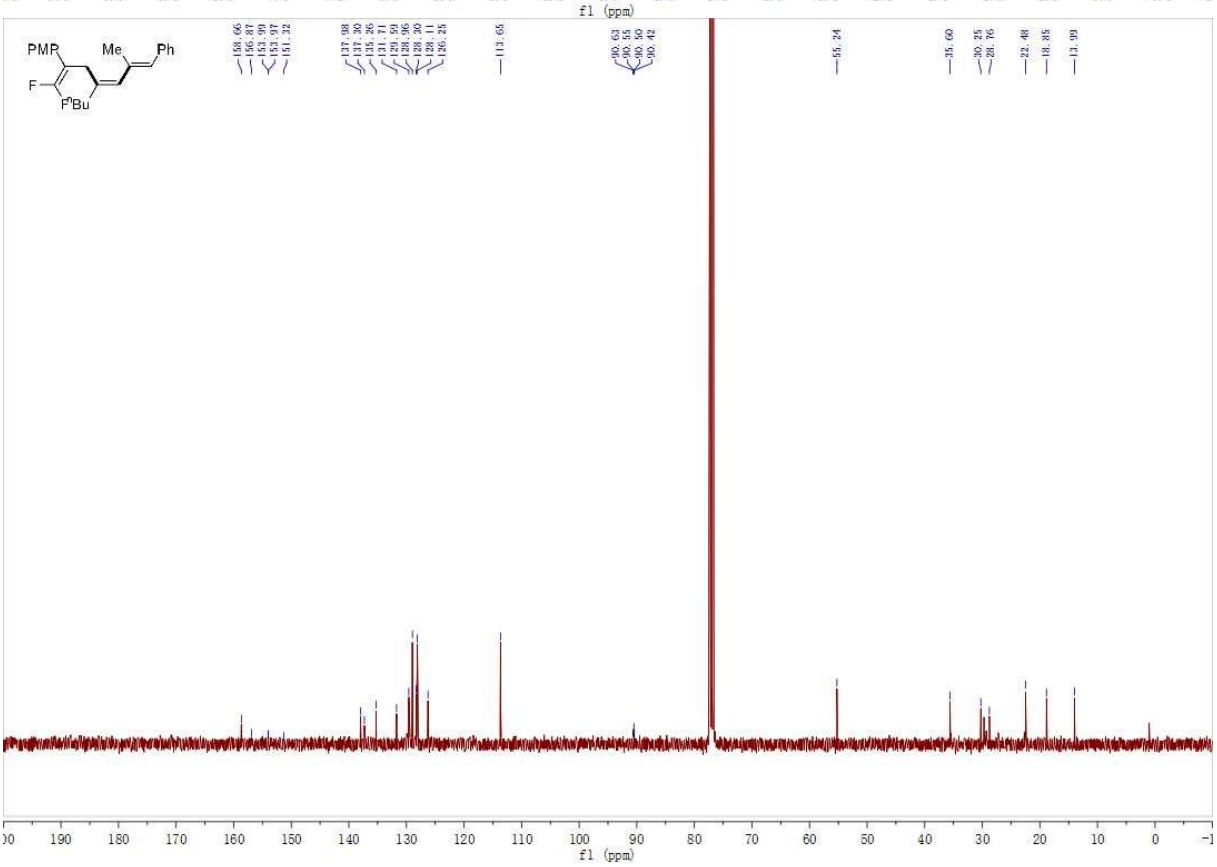
To the **7** (0.1 mmol, 39.2 mg, 1 eq) product in $Pd(PPh_3)_4$ (11.55 mg, 0.1 eq) and THF (2 mL) and H_2O (1 mL) was added K_3PO_4(0.3 mmol, 63.6 mg, 3 eq) and alkenyl boronates **(**0.2 mmol, 48.3 mg, 2 eq**).** The resulting mixture was stirred at 80 ℃ for 8 h. The resulting mixture was quenched with brine. The mixture was extracted with ethyl acetate and the combined organic layer was dried over Na_2SO_4. Then the orgnic layer was concentrated and The residue was purified by columnchromatography with hexane to give **8** as a thick oil (25.6 mg, 67 %).

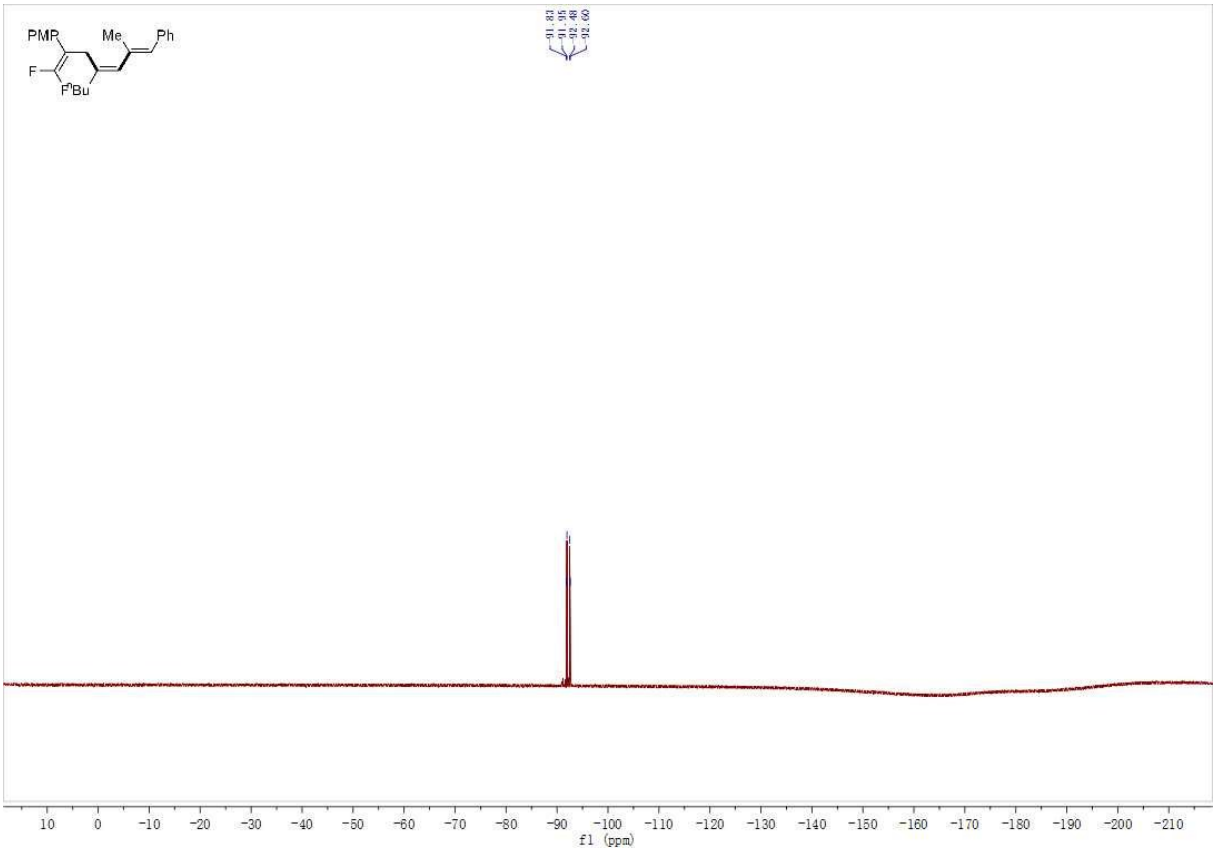
1-((Z)-1,1-difluoro-4-((E)-2-methyl-3-phenylallylidene)oct-1-en-2-yl)-4-methoxybenzene (8)

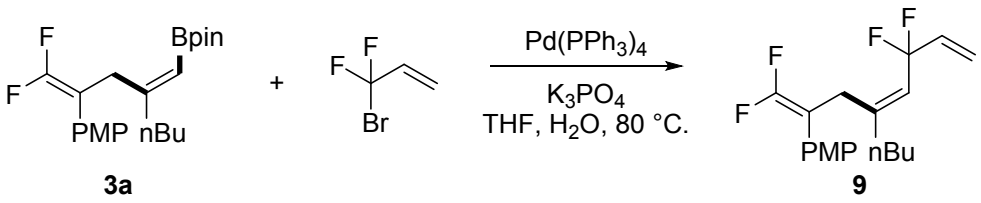


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.24 (m, 3H), 7.18 - 7.05 (m, 4H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.09 (s, 1H), 5.72 (s, 1H), 3.73 (s, 3H), 3.35 (s, 2H), 2.05 (t, *J* = 7.6 Hz, 2H), 1.70 (s, 3H), 1.45 - 1.31 (m, 2H), 1.30 - 1.15 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.66, 154.04 (dd, *J* = 280.3, 278.2 Hz), 137.98, 137.30, 135.26, 131.71, 129.59, 128.96, 128.30, 128.11, 126.25, 113.65, 90.52 (dd, *J* = 13.3, 8.3 Hz), 55.24, 35.60, 30.25, 28.76, 22.48, 18.85, 13.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.89 (d, *J* = 45.0 Hz), -92.54 (d, *J* = 45.0 Hz). HRMS (ESI^+): Calcd for $C_{25}H_{28}F_2O$ $[Na]^+$: 405.2006, Found: 405.2020.


PMP
Me
Ph
F
PBu
f1 (ppm)

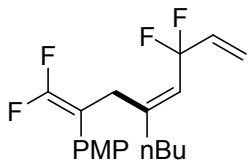

PMP
Me
Ph
F
PBu
f1 (ppm)



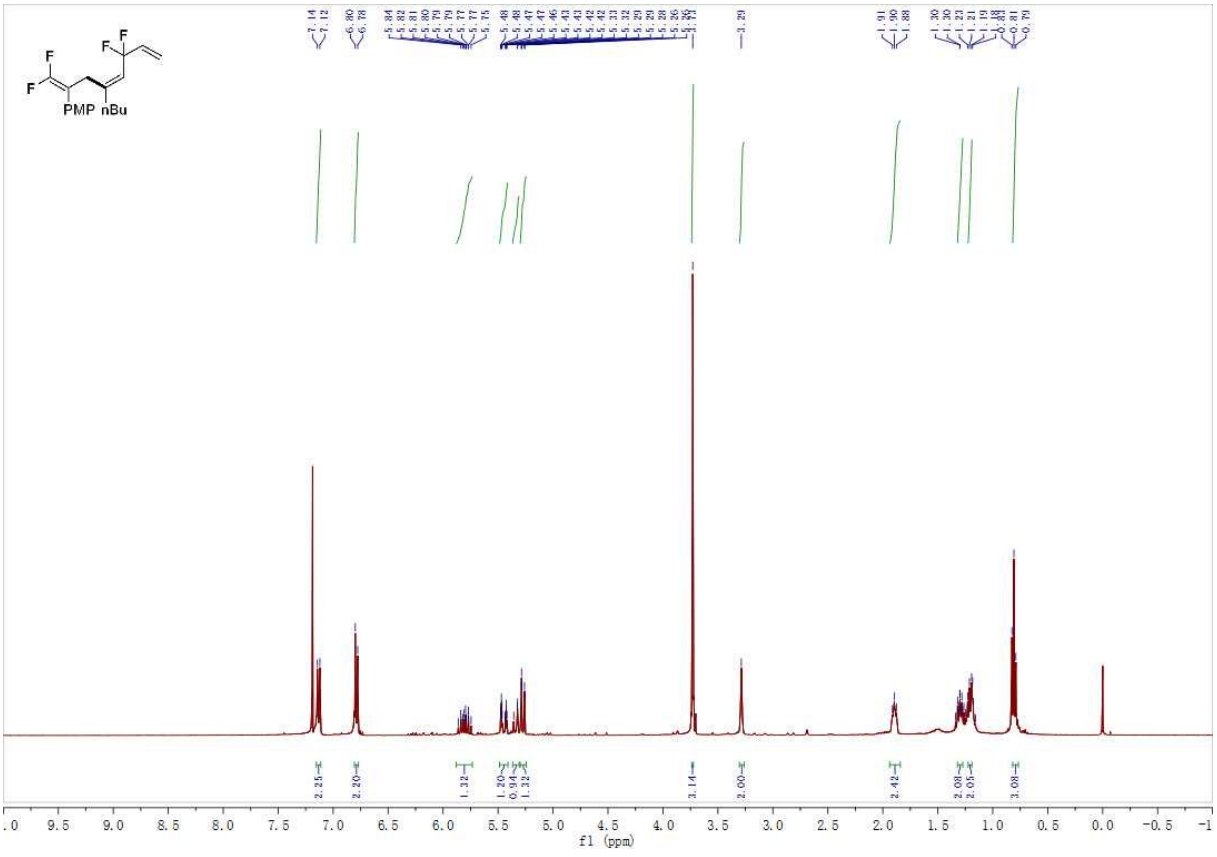


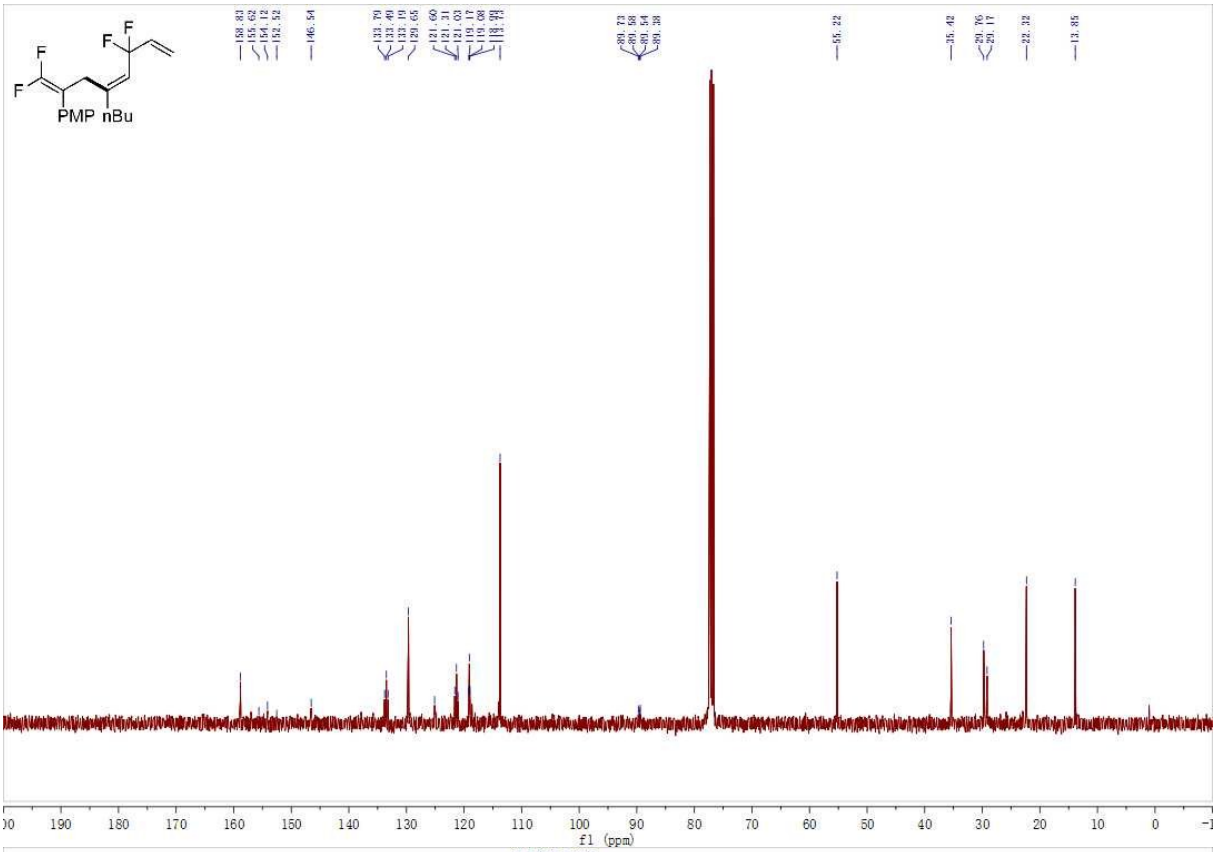
According to the reported literature[2], **9** were conveniently synthesized under slightly modifiedreaction conditions. To the **3a** (0.2 mmol, 78.4 mg, 1 eq) product in $Pd(PPh_3)_4$ (11.6 mg, 0.05 eq) and THF (2 mL) and H_2O (1 mL) was added K_3PO_4 (0.6 mmol,127.2 mg, 3 eq) and 3-bromo-3,3-difluoroprop-1-ene (0.3 mmol, 46.8 mg, 1.5 eq). The resulting mixture was stirred at 80 ℃ for 8 h. The resulting mixture was quenched with brine. The mixture was extracted with ethyl acetate and the combined organic layer was dried over Na_2SO_4. Then the orgnic layer was concentrated and The residue was purified by columnchromatography with hexane to give the **9** as a thick oil (41 mg, 60%).

(Z)-1-(4-butyl-1,1,6,6-tetrafluoroocta-1,4,7-trien-2-yl)-4-methoxybenzene (9)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 5.88 - 5.73 (m, 1H), 5.50 - 5.40 (m, 1H), 5.37 - 5.30 (m, 1H), 5.29 - 5.25 (m, 1H), 3.73 (s, 3H), 3.29 (s, 2H), 1.89 (t, *J* = 7.2 Hz, 2H), 1.36 - 1.25 (m, 2H), 1.23 - 1.15 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.83, 154.13 (dd, *J* = 289.4, 287.1 Hz), 146.54, 133.49, 129.65, 125.11, 121.31, 119.08, 118.68, 113.73, 89.56 (dd, *J* = 20.4, 14.8 Hz), 55.22, 35.42, 29.76, 29.17, 22.32, 13.85. ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.99 (s), -90.94 (d, *J* = 42.7 Hz), -91.04 (d, *J* = 42.7 Hz). HRMS (ESI^+): Calcd for $C_{24}H_{26}BF_3O_2$ $[H]^+$: 343.1685, Found: 343.1689.




F
F
F
F
PMP nBu
158.83
155.62
154.12
152.52
146.54
133.79
133.49
133.19
129.65
121.60
121.31
121.03
119.17
119.08
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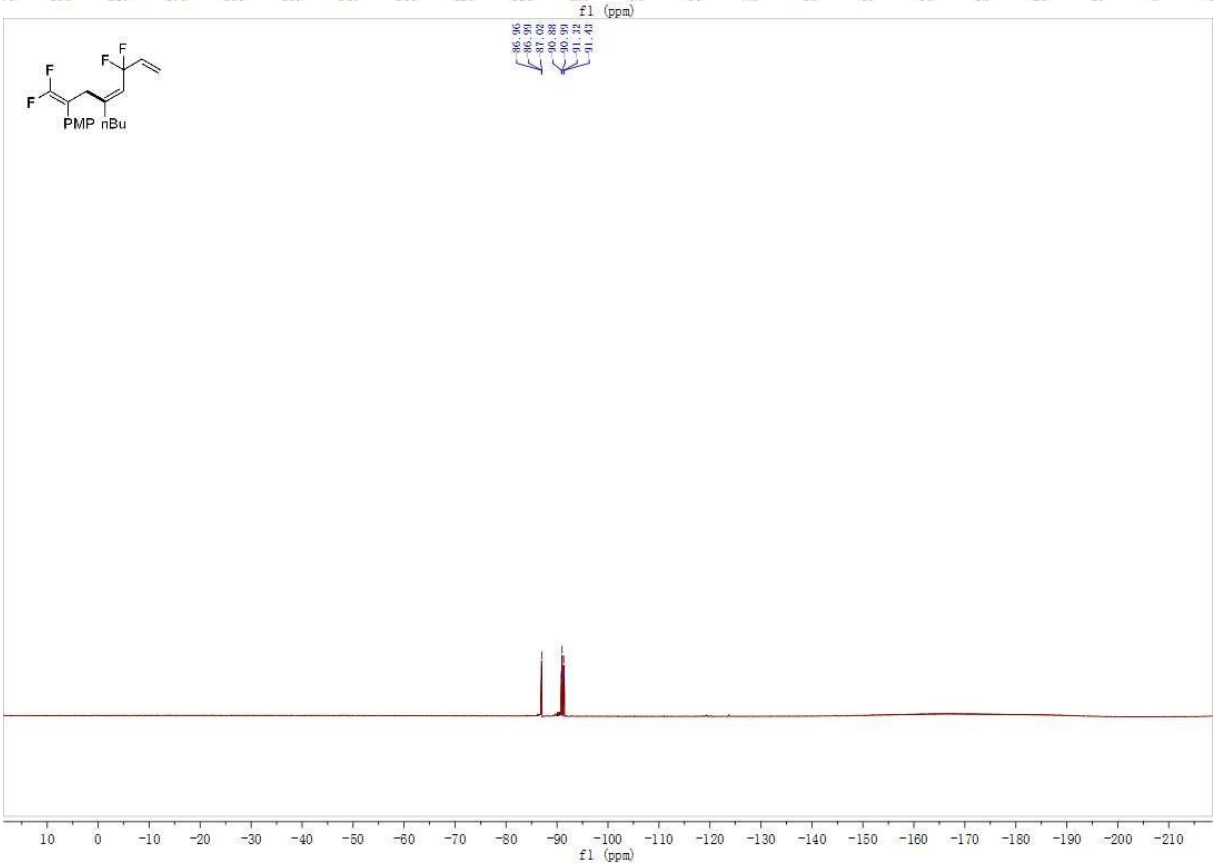
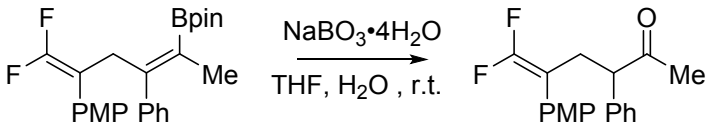
29.76
29.17
22.32
13.85
f1 (ppm)

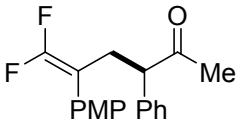

F
F
F
F
PMP nBu
86.96
86.91
87.02
90.88
90.99
91.32
91.43
f1 (ppm)



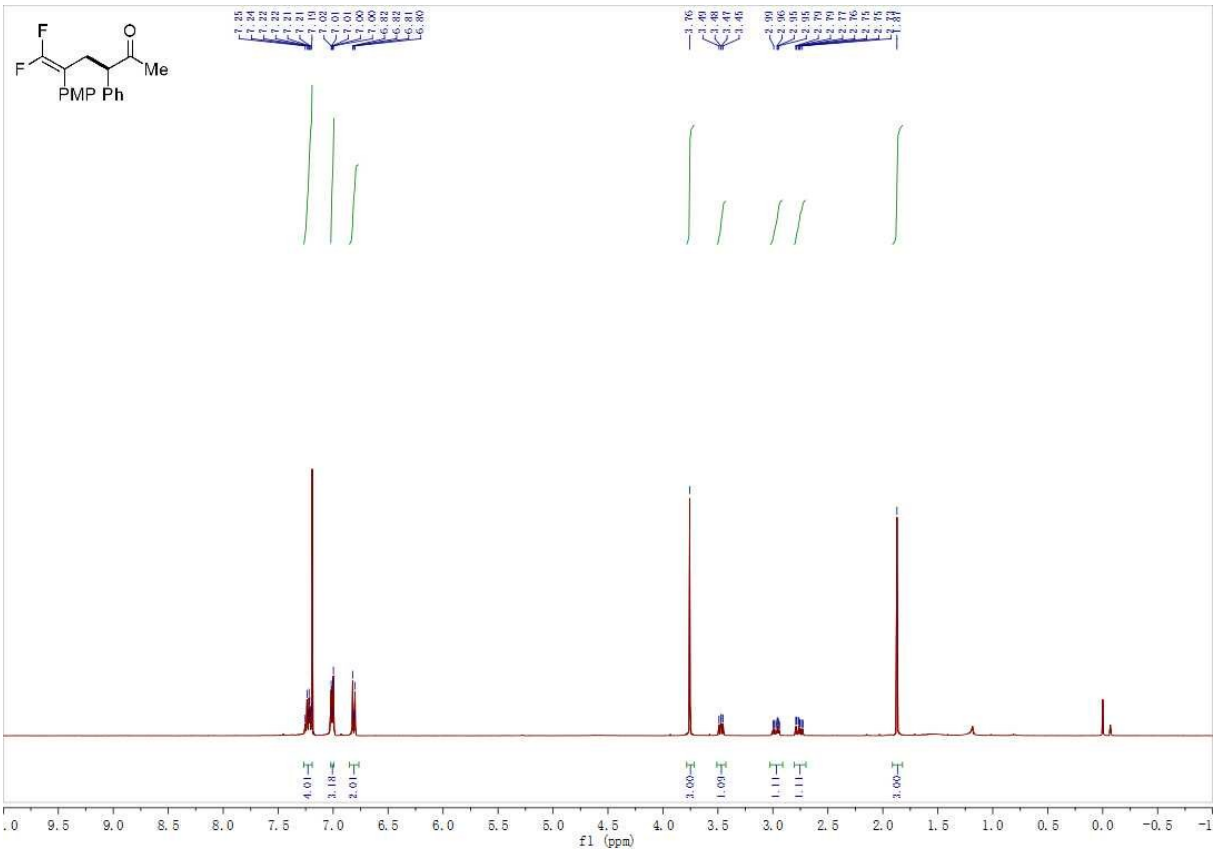
3o **10**

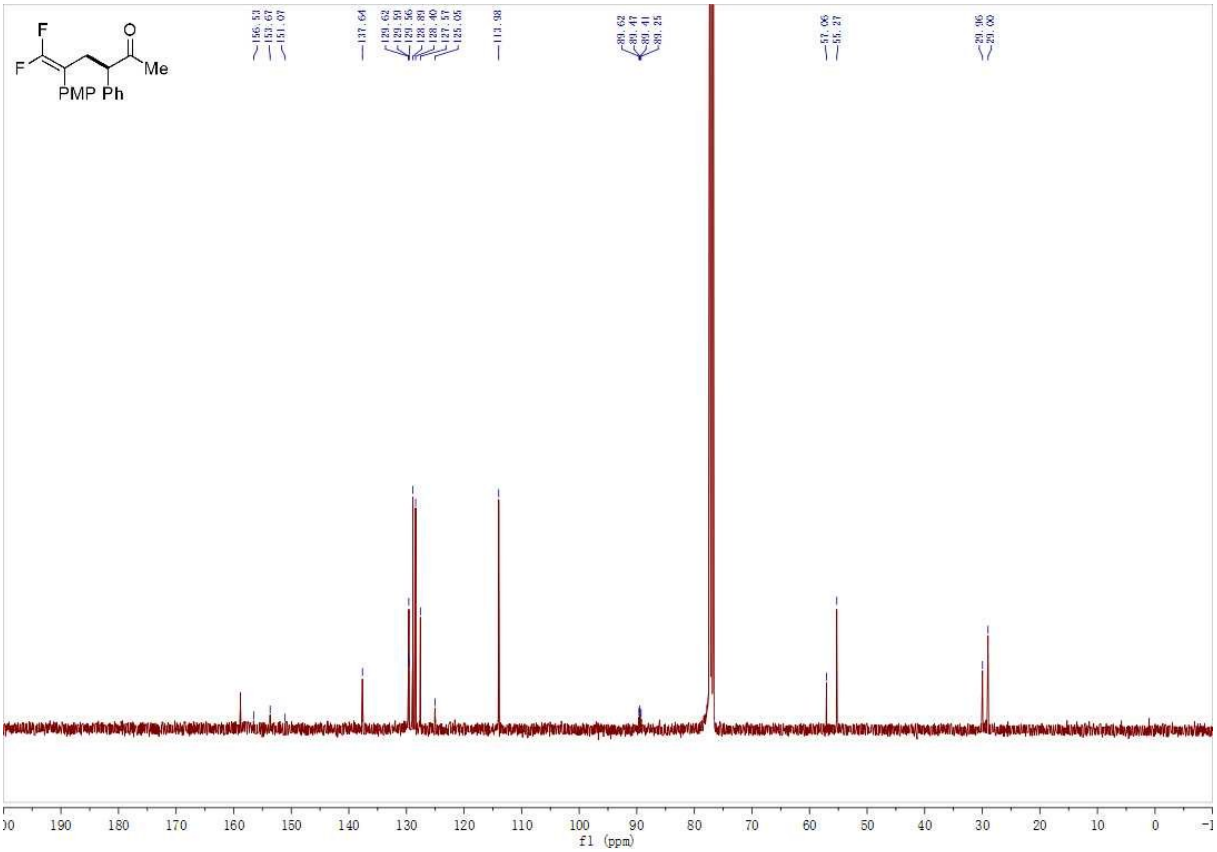
Oxidation of **3o** were performed accoding to the literature[3]. To the **3o** (0.2 mmol, 85.2 mg, 1 eq) product in THF (2 mL) and H_2O (2 mL) was added $NaBO_3 \cdot 4H_2O$ (0.6 mmol, 92.32 mg, 3 eq). The resulting mixture was stirred at room temperature for 20 min. The resulting mixture was quenched with brine. The mixture was extracted with ethyl acetate and the combined organic layer was dried over Na_2SO_4. Then the orgnic layer was concentrated and The residue was purified by columnchromatography with hexane/ethyl acetate (30:1) to give the title compound as a thick oil (51.2 mg, 81 %).

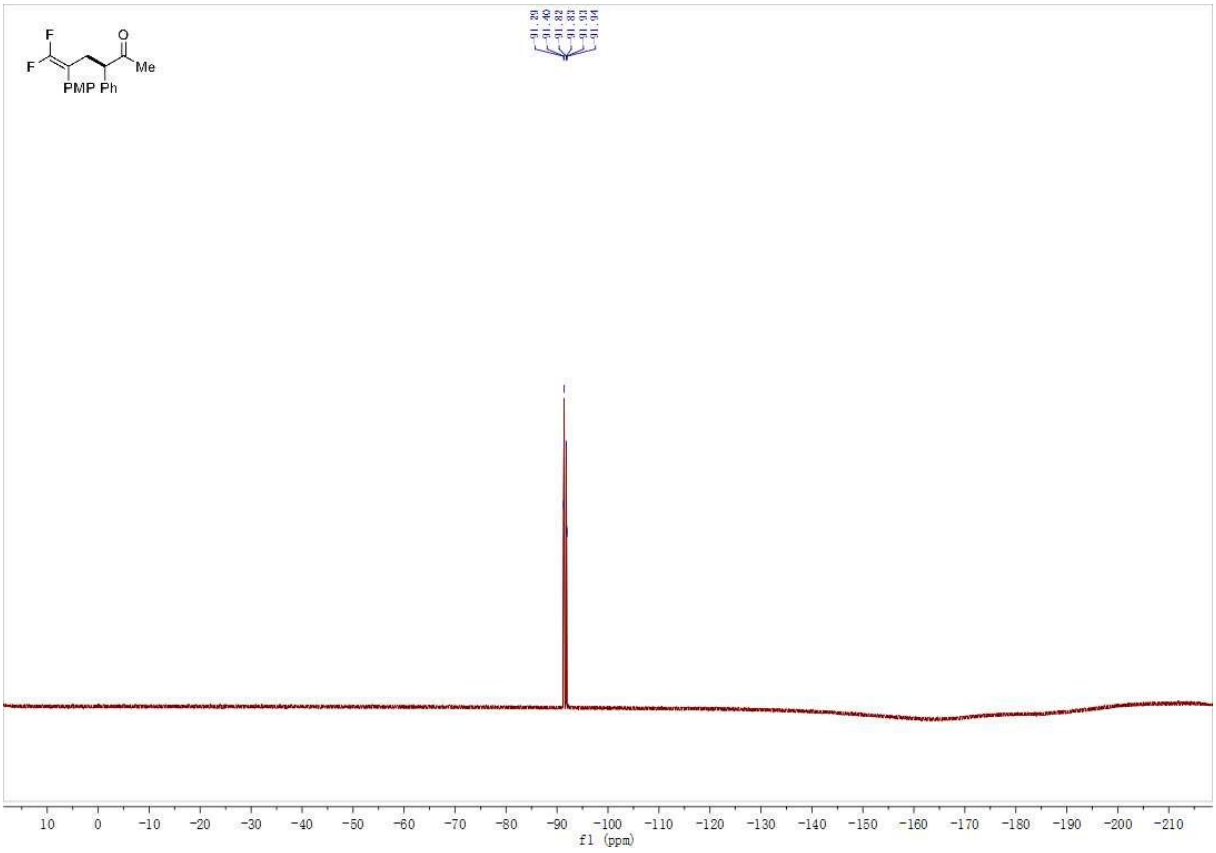
(R)-6,6-difluoro-5-(4-methoxyphenyl)-3-phenylhex-5-en-2-one (10)

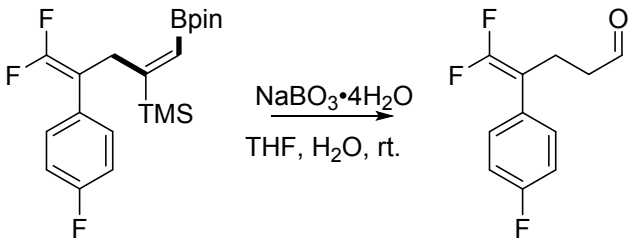


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.19 (m, 4H), 7.03 - 6.98 (m, 3H), 6.84 - 6.79 (m, 2H), 3.76 (s, 3H), 3.51 - 3.44 (m, 1H), 3.02 - 2.93 (m, 1H), 2.80 - 2.72 (m, 1H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.45, 158.83, 153.76 (dd, J = 288.86, 284.86 Hz), 137.64, 129.59, 128.89, 128.40, 127.57, 125.05, 113.98, 89.44 (dd, J = 21.6, 15.7 Hz), 57.06, 55.27, 29.96, 29.00. ^{19}F NMR (376 MHz, $CDCl_3$) δ -91.35 (d, J = 42.7 Hz), -91.88 (d, J = 42.7 Hz). HRMS (ESI^+): Calcd for $C_{19}H_{18}F_2O_2$ $[Na]^+$: 339.1173, Found: 339.1166.


F
F
O
Me
PMP Ph
f1 (ppm)


F
F
O
Me
PMP Ph
f1 (ppm)

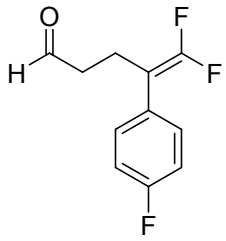




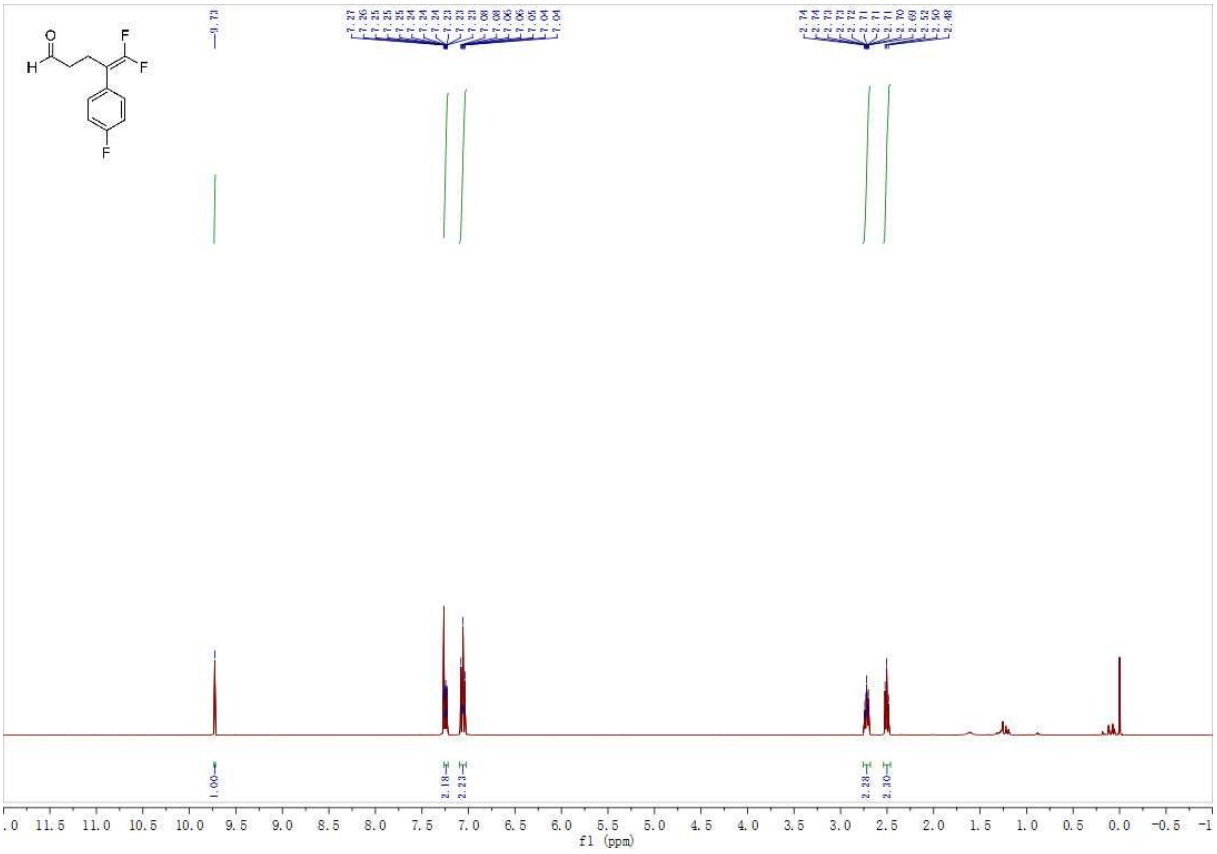
4o

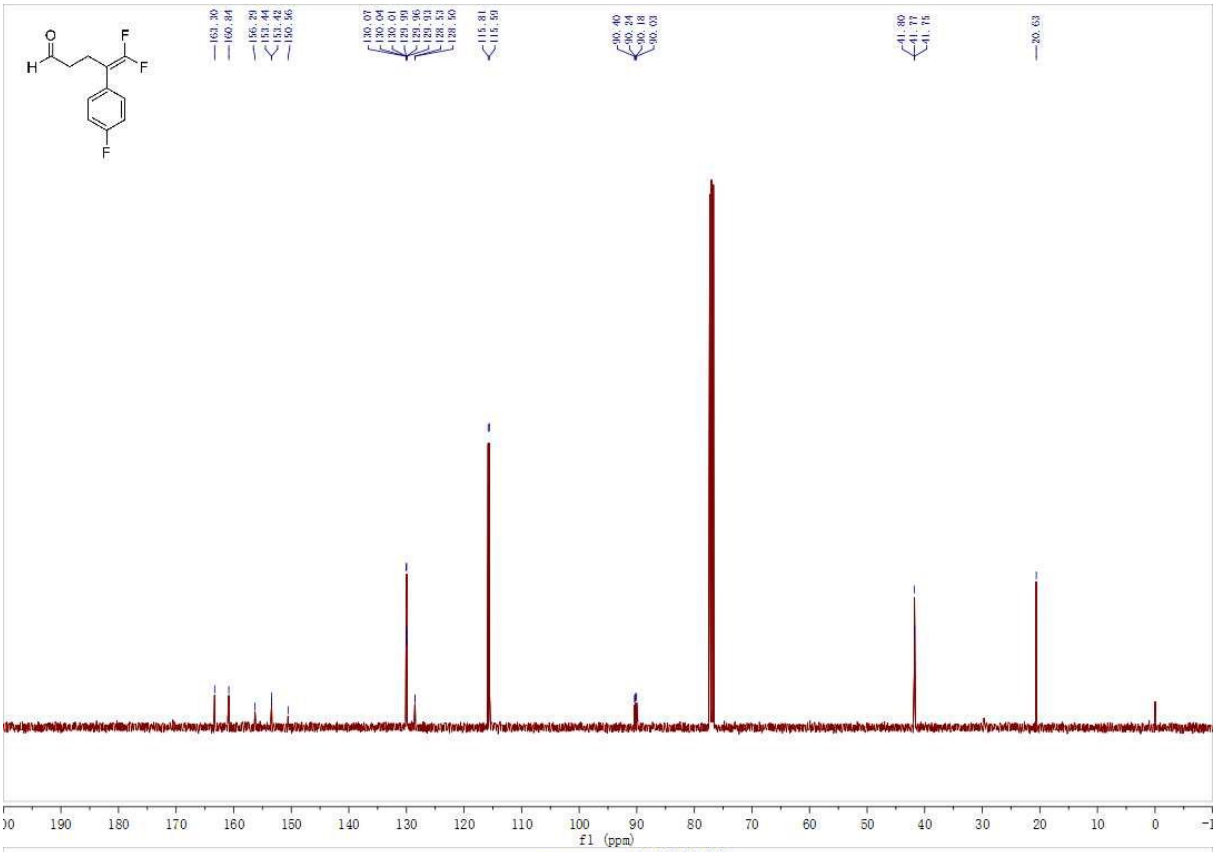
To the **4o** (0.5 mmol, 198.1 mg, 1 eq) product in THF (3 mL) and H_2O (3 mL) was added $NaBO_3 \cdot 4H_2O$ (1 mmol, 153.8 mg, 2 eq). The resulting mixture was stirred at room temperature for 10 min. The resulting mixture was quenched with brine. The mixture was extracted with ethyl acetate, and the combined organic layer was dried over Na_2SO_4. Then the orgnic layer was concentrated and The residue was purified by columnchromatography with hexane/ethyl acetate (30:1) to give the aldehyde as a thick oil (85 %, 91 mg).

5,5-difluoro-4-(4-fluorophenyl)pent-4-enal



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.28 - 7.22 (m, 2H), 7.11 - 7.00 (m, 2H), 2.97 - 2.58 (m, 2H), 2.50 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.66, 162.07 (d, *J* = 247.6 Hz), 153.43 (dd, *J* = 289.4, 287.7 Hz), 129.99, 128.50, 115.70 (d, *J* = 21.6 Hz), 90.21 (dd, *J* = 21.7, 15.5 Hz), 41.77, 20.63. ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.28 (d, *J* = 41.5 Hz), -90.53 (d, *J* = 41.5 Hz), -113.96 (s). HRMS (ESI^{+}): Calcd for $C_{11}H_9F_3O$ [H]$^{+}$: 215.0684, Found: 215.0687.




O
H
F
F
F
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160.84
156.29
153.44
153.42
150.56
130.07
130.04
130.01
129.99
129.96
129.93
128.53
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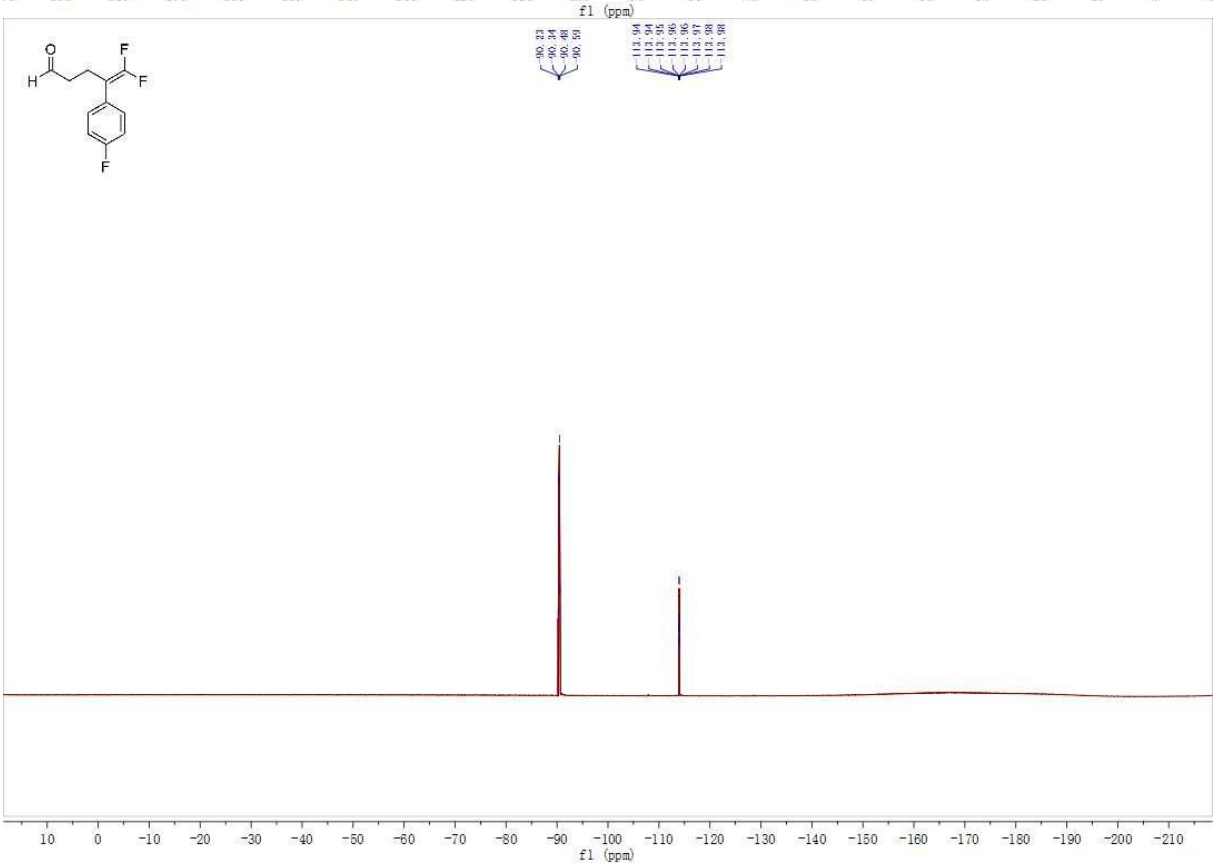
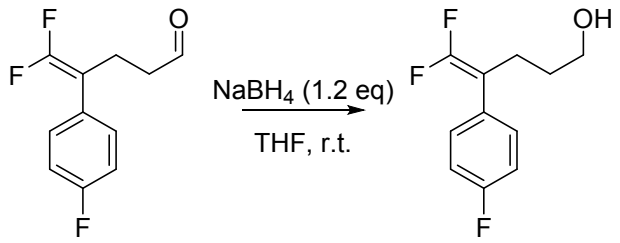
90.03
41.80
41.77
41.75
20.63
f1 (ppm)

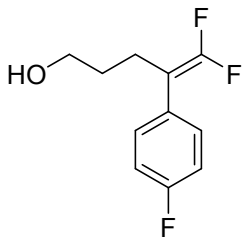

O
H
F
F
F
-90.23
-90.34
-90.48
-90.59
113.94
113.94
113.95
113.96
113.96
113.97
113.98
113.98
f1 (ppm)



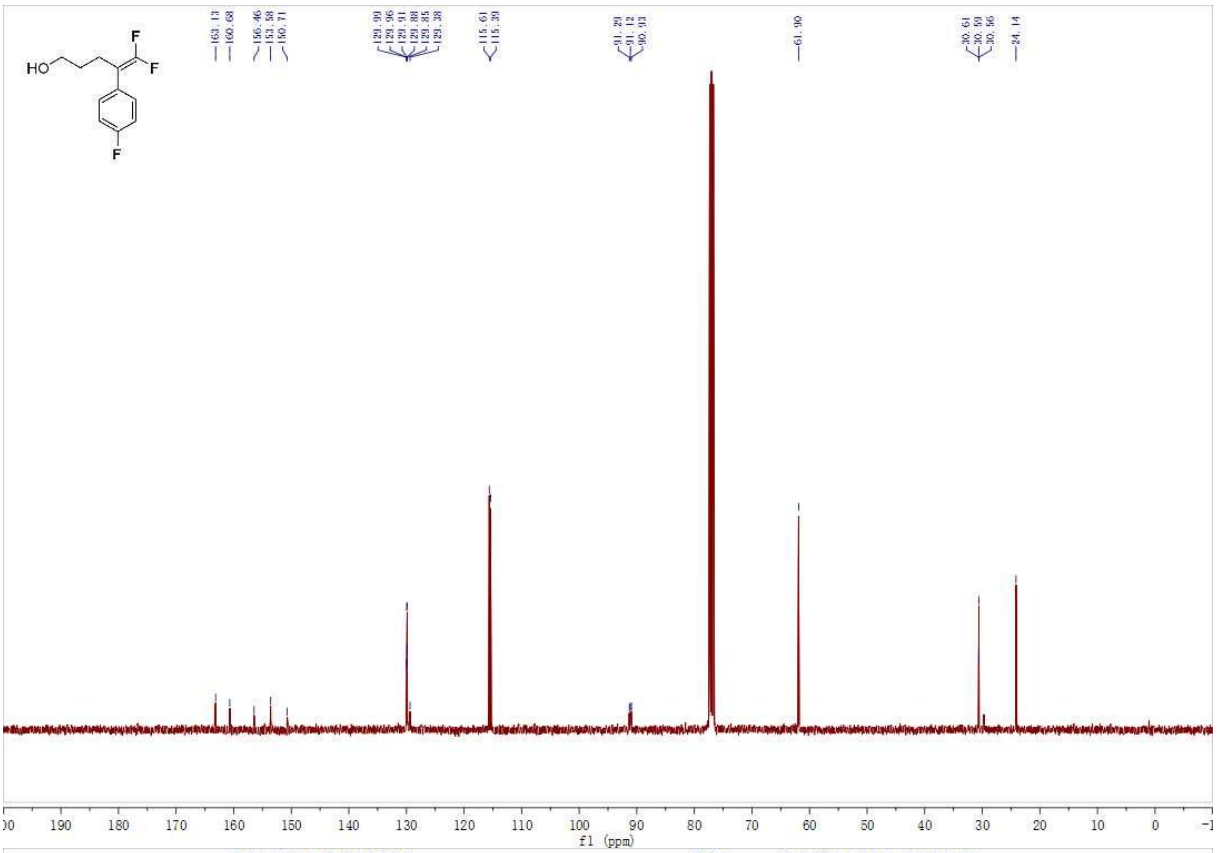
11

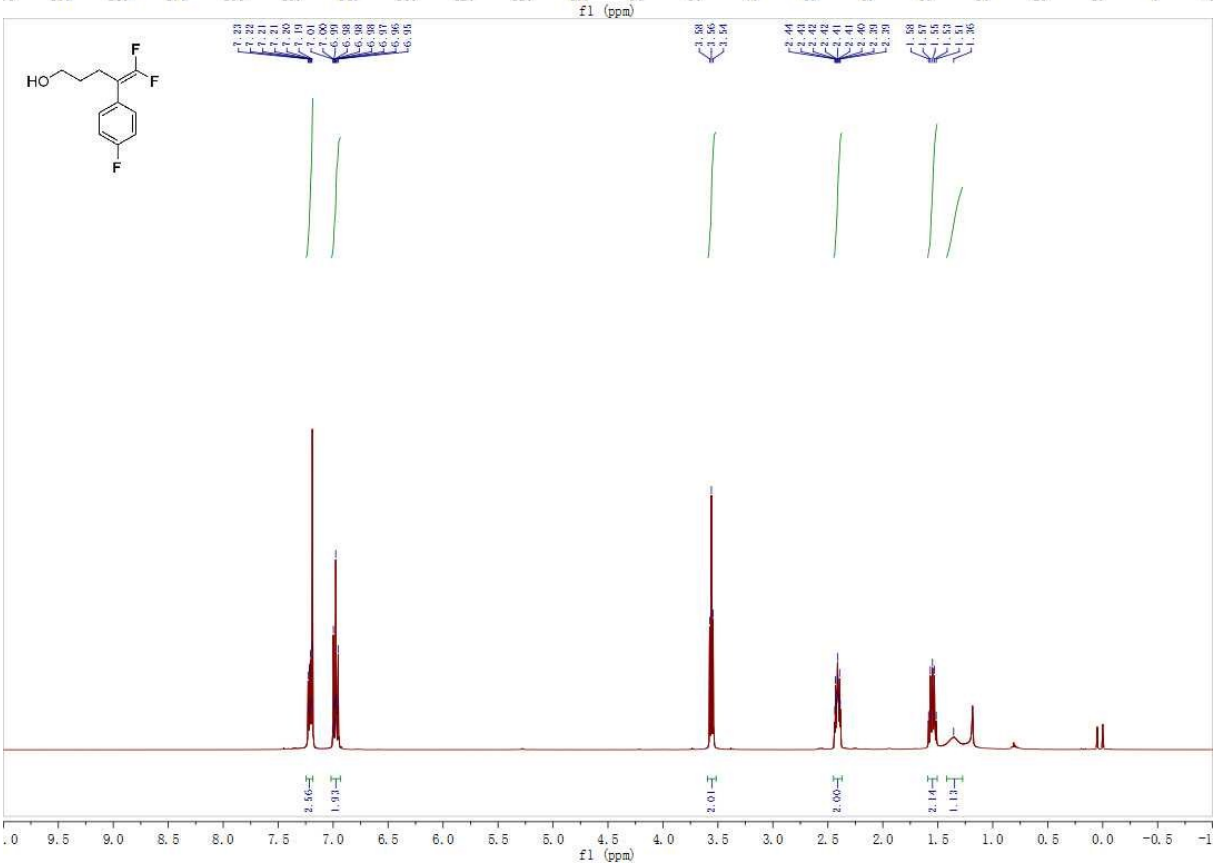
To the solution of the aldehyde (0.2 mmol, 42.8 mg, 1 eq) in THF (1 mL) was added $NaBH_4$ (0.24 mmol, 9 mg, 1.2 eq). The resulting mixture was stirred at room temperature for 3 min. The resulting mixture was quenched with brine. The mixture was extracted with ethyl acetate and the combined organic layer was dried over Na_2SO_4. Then the orgnic layer was concentrated and The residue was purified by columnchromatography with hexane/ethyl acetate (10:1) to give **11** as a thick oil (90 %, 38.9 mg).

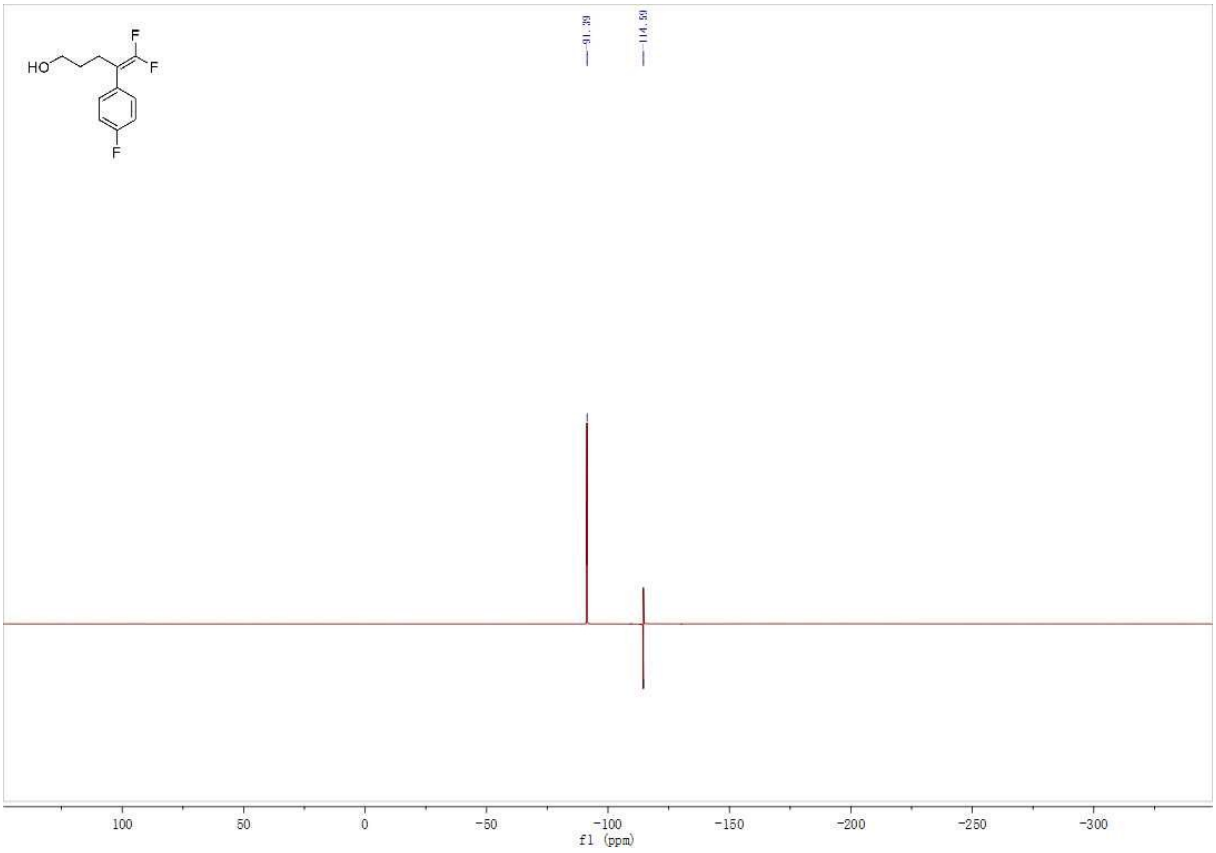
5,5-difluoro-4-(4-fluorophenyl)pent-4-en-1-ol (11)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.16 (m, 2H), 7.04 - 6.91 (m, 2H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.53 - 2.31 (m, 2H), 1.64 - 1.46 (m, 2H), 1.36 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.91 (d, *J* = 247.0 Hz), 153.58 (dd, *J* = 290.88, 289.87 Hz), 129.91, 129.38, 115.50 (d, *J* = 21.6 Hz), 91.11 (dd, *J* = 19.2, 16.6 Hz), 61.90, 30.59, 24.14. ^{19}F NMR (377 MHz, $CDCl_3$) δ -91.39, -114.59. HRMS (ESI^+): Calcd for $C_{11}H_{11}F_3O$ $[Na]^+$: 239.0660, Found: 239.0654.

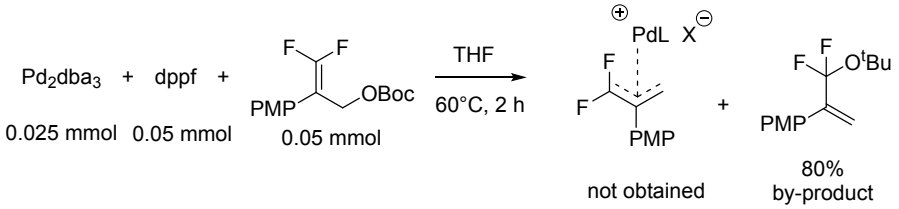

HO
F
F
F
f1 (ppm)


HO
F
F
F
2.56
1.93
2.01
2.00
2.14
1.13
f1 (ppm)

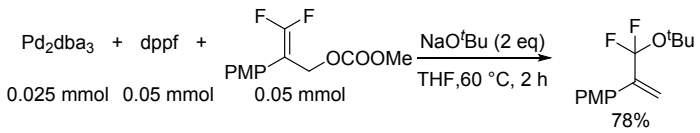


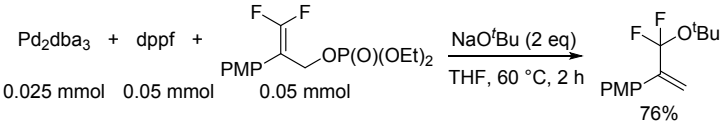
Proposed reaction mechanism.

We designed the following mechanism experiments to prepare the Pd species, regrettably, we did not get the Pd species, but we obtained the C(F_2)-O cross-coupling by-product in 80% yield.



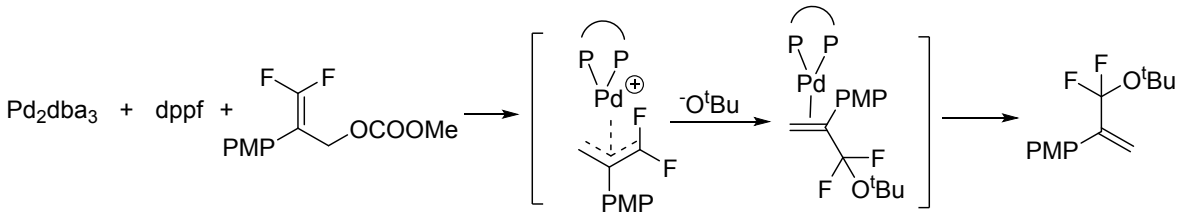
Then, other 3,3-difluoro-substituted allylic esters (**2b, 2c**) were used, C(F_2)-O cross-coupling product were observed in 78% and 76% yields, respectively. It's noticed that, the reaction was take place at CF_2 site.



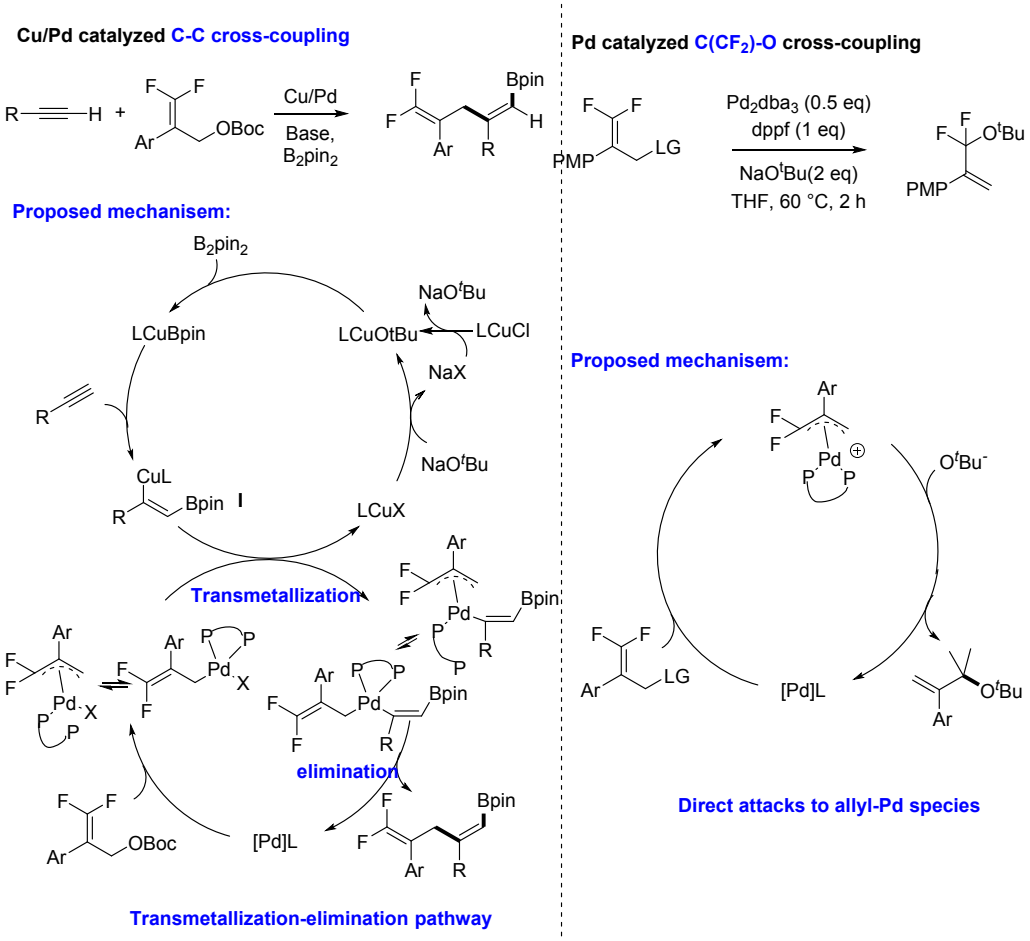


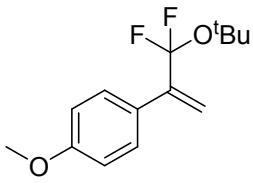
General procedures: To a Schlenk tube equipped with a magnetic stir bar were added Pd_2dba_3 (0.025 mmol), dppf (0.05 mmol), 3,3-difluoro-substituted allylic esters (0.05 mmol) and THF (0.5 mL). The resulting solution was stirred at room temperature for 1 h. Then NaO^tBu (0.05 mmol) was added to the mixture. The resulting solution was stirred at room temperature for 2 h. After this time, then reaction was cooled to room temperature. Et_2O and water were added and the layers were separated. The aqueous phase was extracted with Et_2O (x 2) and the combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel to give the product.

Based on previous work[4], a proposed mechanism was shown for the formation of the by-product. Pd(η3-p-allyl)(X)(dppf) was formed firstly, then soft nucleophile -O^{t}Bu directly attacks to η3-allyl-Pd species afford the C-O coupling product. The process go through the following mechanism:

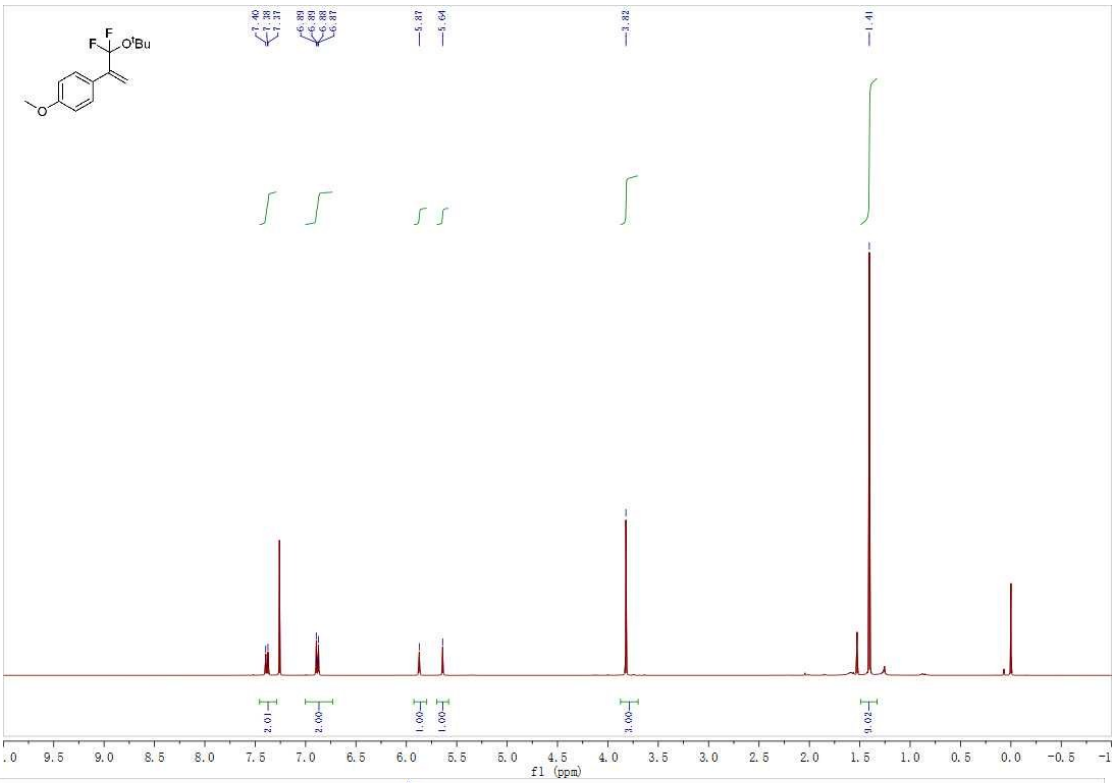


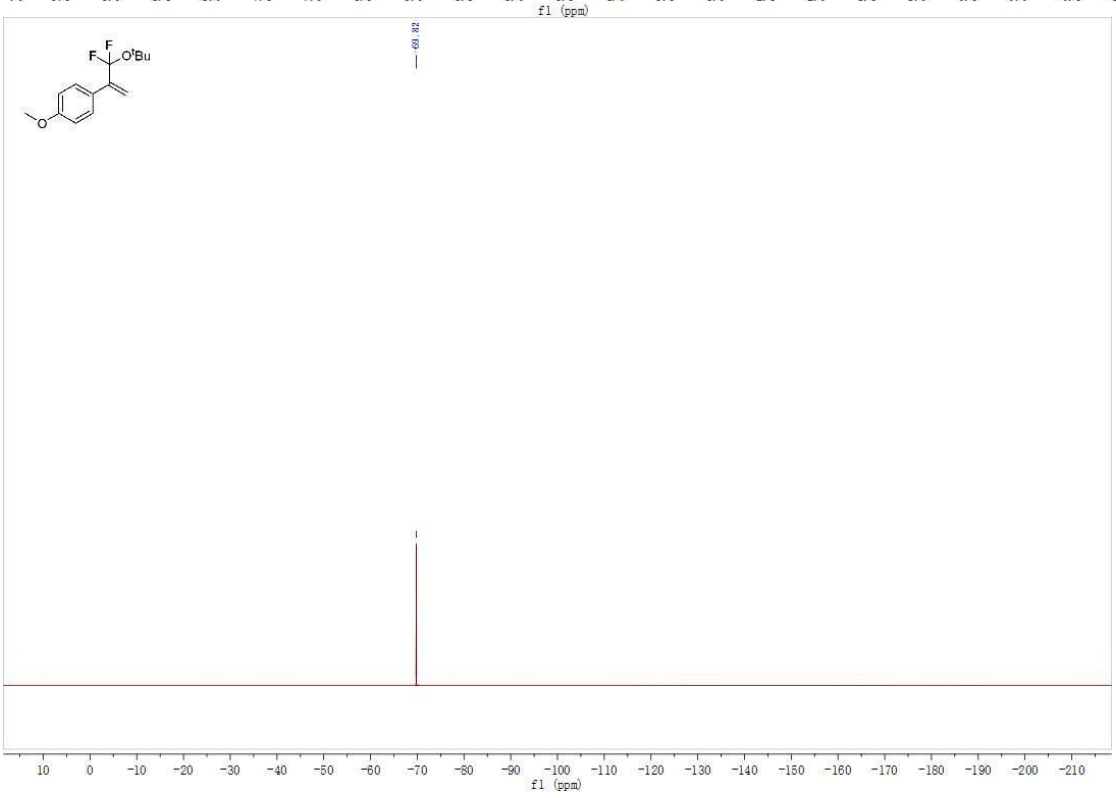
However, in the Cu/Pd catalyzed boryldifluoroallylation, C-C bond formation occur at CF_2 site, and this result is contrast with the findings of above mentioned C-O cross-coupling. The difference in reaction mechanism may be the reason for the selectivity of these two sites. A proposed mechanism was shown as follows[5]: First, regio- and stereoselective borylcupration of the alkyne with LCu-Bpin complex would catalytically generate borylalkenylcopper intermediate. Meanwhile, a π-allyl Pd(II) complex would be formed by oxidative addition of an allyl substrate to a Pd(0) complex. Then, transmetalation between borylalkenylcopper intermediate and Pd(II) complex afford new Pd-complex. Finally, regioselective C-C reductive elimination formation of the product and regeneration of the catalysts.

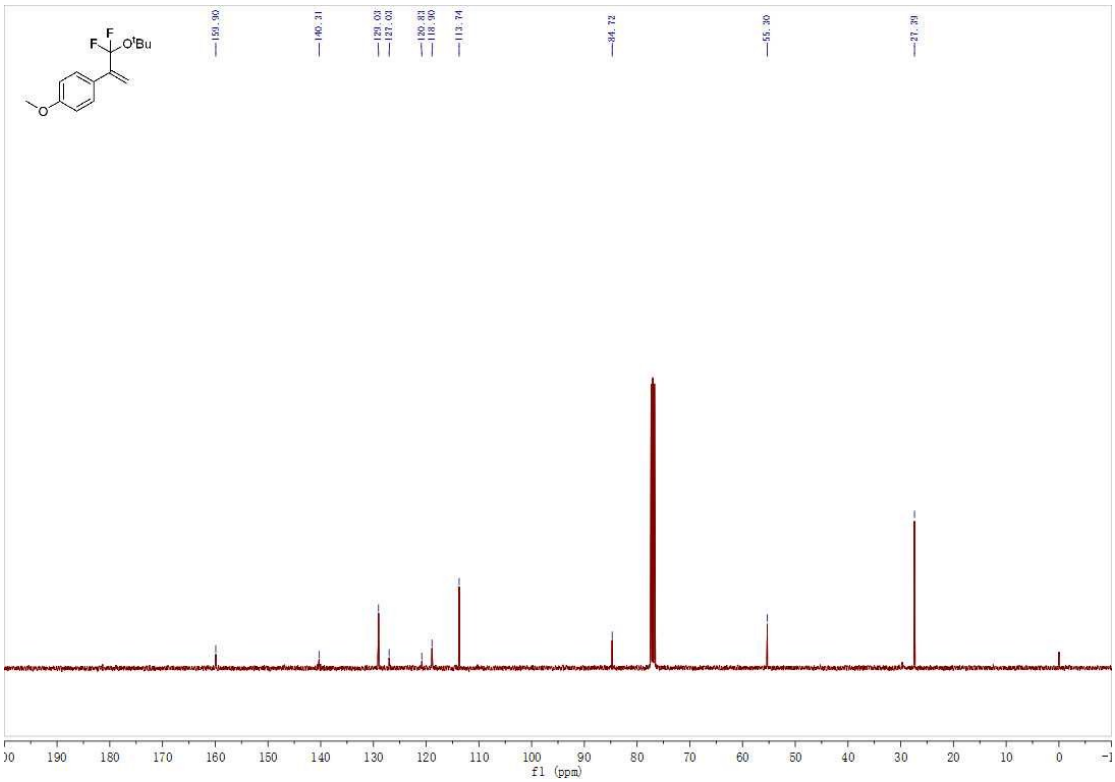




^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 2H), 7.22 – 6.72 (m, 2H), 5.87 (s, 1H), 5.64 (s, 1H), 3.82 (s, 3H), 1.41 (s, 9H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.82 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.90, 140.31, 129.03, 127.03, 120.83, 118.90, 113.74, 84.72, 55.30, 27.39.


F
F
O^{t}Bu
O
7.40
7.38
7.37
6.89
6.89
6.88
6.87
5.87
5.64
3.82
1.41
2.01
2.00
1.00
1.00
3.00
9.02
f1 (ppm)


F
F
O^{t}Bu
O
-69.82
f1 (ppm)



4. References

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